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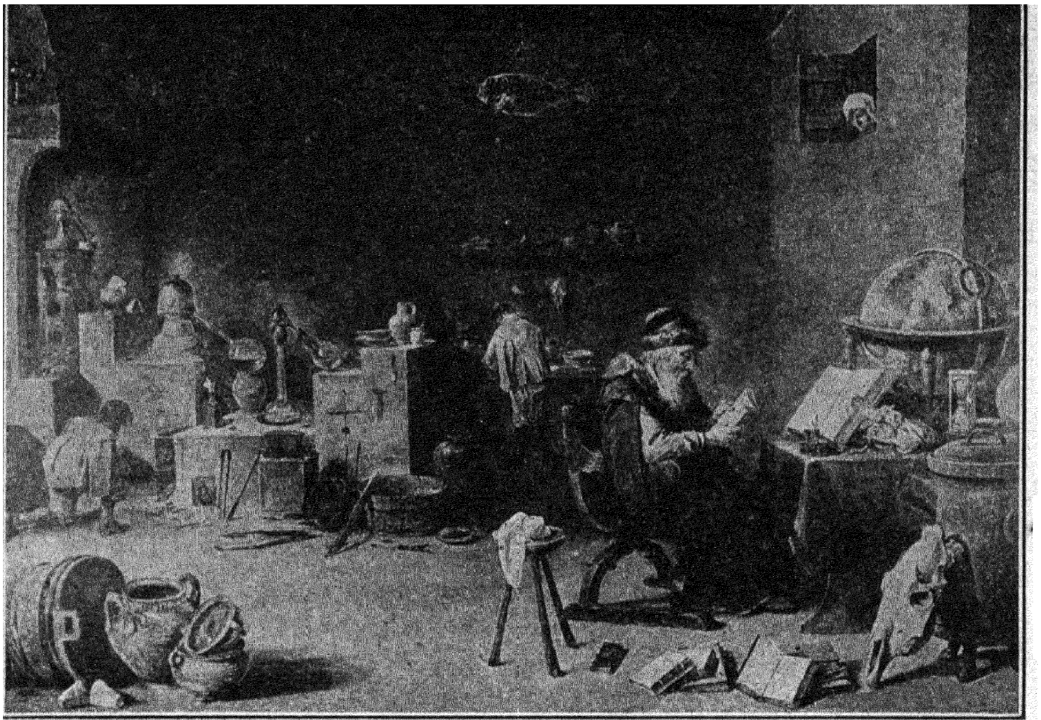
OF
ELEMENTARY ORGANIC CHEMISTRY



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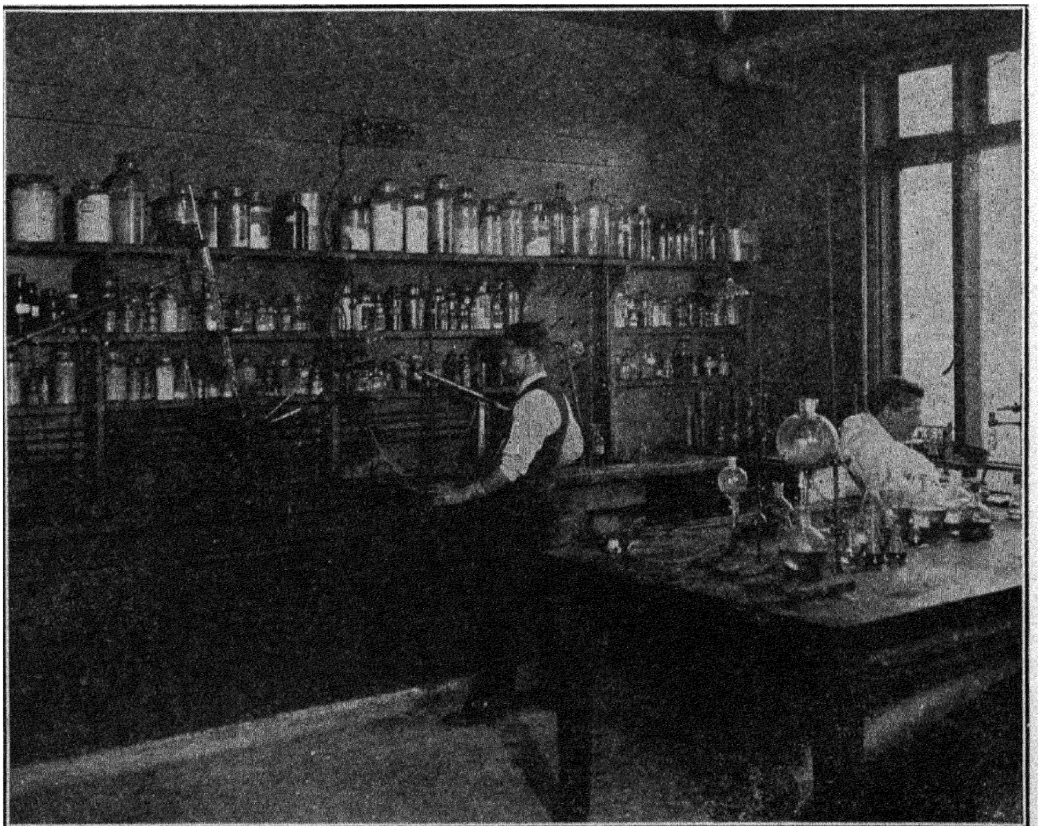

An Organic Research Laboratory in The Mellon Institute of Industrial Research.

A LABORATORY BOOK
OF
ELEMENTARY ORGANIC CHEMISTRY

BY

ALEXANDER LOWY, Ph.D.
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AND
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SECOND EDITION

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AND
WILMER E. BALDWIN

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A LABORATORY BOOK
OF
ELEMENTARY ORGANIC CHEMISTRY

NOTES FOR STUDENTS *

GENERAL DIRECTIONS

Carefully read through the entire experiment before coming to the laboratory, and also familiarize yourself with the theory involved. A total understanding of an experiment can only be obtained by knowing the theory involved as well as the experimental part. *You are expected to have a knowledge of what you are doing at the time you are doing it.*

Follow the laboratory directions carefully. If you are in doubt as to the meaning of any terms or directions, consult the instructor.

Do not follow directions mechanically but know the reason for each step. In other words, know *why* as well as *how*. Remember the good old saying, " There will always be a job for the man who knows *how*, but the man who knows *why* will always be his boss."

Develop your powers of observation and reasoning.

Always bring your text-book to the laboratory. You will need it for reference purposes.

You will frequently have occasion to refer to tables for melting points, boiling points and other physical constants. Books for this purpose are placed in the laboratory and should be consulted.

Record each observation at the time you perform the experiment.

In order to complete the laboratory work assigned for the course it will be necessary to save time wherever possible. Plan your work before coming to the laboratory so that in certain cases more than one experiment can be performed simultaneously.

Certain experiments must be completed or carried to a certain stage during the same laboratory period in which the work is begun. Such experiments should be started at the beginning of the period.

Reactions often take place with explosive violence. Therefore always be cautious in your manipulation.

Mix reagents only as directed. To do otherwise may result in a violent reaction or explosion.

Exactness, neatness and cleanliness are essential to good work and good results.

Each student should provide himself with a laboratory coat or apron as a protection for his clothes.

While working in the laboratory keep your laboratory book in such a position on your desk that no chemicals will be spilled on it. If a sheet is soiled or destroyed, prepare a typewritten duplicate copy.

If the cover of your laboratory book becomes soiled replace it with a new one, and thereby save the binding f the book.

Always work independently unless otherwise directed by the instructor. Work at your own desk.

Take proper care in the use of balances, reagents and other general laboratory equipment.

Do not throw match sticks, paper, or solids into the sinks. Crocks are provided for this purpose.

At the end of the laboratory period sponge off your desk top.

You are held responsible for a knowledge of the material on the direction sheets, results obtained, and answers to questions.

Explanation of certain terms.

Yield—Actual amount (in grams) of compound you prepare.

---

* At the University of Pittsburgh the Student is held responsible for a knowledge of the contents of the " Notes for Students," before he is permitted to begin his laboratory work.

Theoretical yield—Yield which would be obtained if a reaction would go to completion and no side reactions occurred.

$$\text{Per cent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100.$$

Blank sheets are inserted at the end of the book where you can note special directions given during the course.

It is a good policy not to lend or borrow apparatus.

Remember that a noisy laboratory is not conducive to good work.

See with your own eyes, feel with your own hands, taste with your own tongue, write your own words, think with your own mind. In brief—do your own work. Copying your classmate's notes and answers does not develop your faculty of observation or your reasoning power.

NOTES ON EXPERIMENTAL WORK

Never taste any substance unless so directed.

Never look down into a test tube or flask in which you are conducting an experiment. Failure to observe this precaution may result in the loss of an eye.

Do not point the open end of a test tube in which you are heating something toward your own face or toward your neighbor. Remember, he values his face more than you do.

Never hold a test tube in your fingers while heating, but use a test-tube holder.

Many liquids are poisonous or have disagreeable odors. In smelling the vapors from such liquids do not bring the receptacle close to the nose. Gently waft the fumes with the hand toward your nose.

Always use the hood in performing experiments in which objectionable odors are evolved.

Never attempt to extract hot solutions with low boiling-point solvents, such as ether, carbon disulfide, chloroform, benzene, etc.

When evaporating flammable liquids such as alcohol, ether, carbon disulfide, benzene, acetone, petroleum ether, etc., use a hot-water bath or steam bath or an electric hot plate. Have no flames within a radius of at least eight feet from where you are conducting the evaporation. Remember that if you do not observe this precaution, you and your neighbors may be sent to the hospital suffering from severe burns.

Never heat a flask directly with a flame. Always use a wire gauze, asbestos pad, or water bath, depending on the nature of the substance to be heated.

Never heat a test tube, flask, bottle, etc., when the stopper is tightly fitted.

Whenever you are conducting a fusion experiment with NaOH, protect your eyes with goggles and your hands with gloves.

When distilling high-boiling liquids, i.e., those boiling above 200°, use a distilling flask with a low side-arm.

In conducting experiments where flammable liquids are distilled, neighboring students should arrange their apparatus as indicated below.

O	O	O	O	O	O
flame	receiver	receiver	flame	flame	receiver
Student A		Student B		Student C	

Whenever distilling or generating flammable substances always extinguish the flame before disconnecting the apparatus.

The flask from which a liquid is to be distilled should have a volume from one-half to one-third greater than that of the liquid.

When it is necessary to keep a test or preparation until the next laboratory period, always label the container. Do not depend upon your memory for this.

Tests can be obtained just as well with small amounts of substances as with large amounts. Do not get into the habit of wasting materials.

Always test for acidity, alkalinity and neutrality point; do not guess at it.

Gas is expensive, therefore do not waste it. Be sure to shut off the gas and water on your desk before leaving the laboratory at the end of the period.

Warnings are frequently given in the laboratory directions. Observe these closely. Remember in failing to do so you are not only endangering yourself, but also your neighbors.

Release stopper of separatory funnel gradually after shaking any volatile liquid such as ether, chloroform, etc.

NOTES ON APPARATUS

Set up apparatus carefully and in accordance with the laboratory directions. It should be inspected by the instructor before you actually begin work. Any changes should be attended to immediately.

Always use the size of apparatus specified.

Replace broken apparatus immediately so that your equipment is always kept up to standard.

No apparatus except that in actual use should be allowed to collect on the desk top.

Keep apparatus clean. Only clean glassware should be used. Frequently erroneous results are obtained by using unclean apparatus. You should provide yourself with a sponge, a bar of soap, a towel and some scouring powder. If you cannot clean your apparatus by any other means, allow it to remain in contact with the cleaning solution. This may be made up as follows:—To 250 cc. of commercial H_2SO_4 add 50 g. of commercial sodium dichromate, warm gently, and after cooling transfer to bottle.

After washing out tubes, flasks, or beakers, invert so that they will drain.

In many tests and preparations dry vessels must be used, otherwise erroneous results may be obtained. If glassware is not dry, rinse thoroughly with a small amount of alcohol, and then with a small amount of ether. Pour these reagents into receptacles provided for this purpose.

When measuring a few cubic centimeters of a liquid use a 10 cc. graduate

Use rubber stoppers only where specified.

When using stoppers select one such that one-fourth of it fits in the flask.

All corks should be bored so that glass tubing, thermometer, or side-arm of distilling flask fits tightly. In boring corks select a cork-borer of such a size that its diameter is slightly less than that of the tube, side-arm, or thermometer over which it is to fit. To bore a hole in a cork, hold it in your hand, place the cork-borer at the middle of one end of the cork, and bore part way through. Then place the borer at the middle of the other end and bore the remainder through. Keep the borer and cork straight. Use a rotating motion in boring; do not attempt to push the borer through the cork. Never rest the cork on the desk top; to do so may result in dulling the knife-like edge of the borer, thus rendering it useless. A file should be used to smooth off the rough edges of the hole. In fitting a tube or thermometer into a cork, never attempt to push it in. This may result in broken glass and a badly cut hand. Gradually work the cork on by means of a rotating motion. Moistening the cork will aid in this operation.

Keep your burner in good condition. Be sure that you understand its mechanism so as to obtain the best source of heat.

Flasks, tubes, and condensers should be clamped as illustrated in Figs. 1, 8, 9, 16, 22, 25, 37. Never clamp a piece of apparatus tightly. Allowance must be made for the expansion of glass on heating.

The terms " reflux condenser " and " reflux air condenser " are frequently used in the laboratory directions. The reflux condenser is the water condenser set up in an upright position with water running through it. The reflux air condenser is the air condenser (inner condenser tube) set up in an upright position.

A very thin film of vaseline or stop-cock grease should be smeared on the stop-cocks of separatory and dropping funnels so that they will turn easily. If a stop-cock sticks at any time take the funnel to the stock room, where a device is kept for loosening same, and observe how it is done. The stop-cock should always be held in position by a rubber band.

See that the filter paper you use fits your Büchner funnel.

The Büchner funnel should be used only for filtration by suction. It should be fitted to the neck of the suction flask by means of a rubber stopper.

Thermometers should be allowed to cool gradually. Never hold a hot thermometer under the cold-water faucet, for it will cost you the price of a new one.

Do not use glass tubing, spatula, or pestle for stirring. Use glass rods which have been rounded off at the ends by holding in a flame.

To connect two pieces of glass tubing, draw a short piece of rubber tubing partly over the end of one piece of the glass tubing. Then insert the other piece until the ends of the two pieces of glass tubing are almost in contact.

The stop-cock of a separatory funnel should always be held in place by means of a rubber band.

If you are interested in seeing the various industrial equipments illustrated in this book, you will find them in industrial chemistry or chemical engineering laboratories.

NOTES ON CHEMICALS

Use the reagents at the reagent shelf. Never take them to your desk. Do not put an empty reagent bottle back on the shelf but hand it to the instructor to be refilled.

Do not attempt to transfer a solid reagent directly from a bottle to a test tube. First place the solid on a piece of paper. Then make a trough out of the paper and transfer the solid to the test tube.

Never pour excess reagents back into the reagent bottles. To do so may result in contamination of the reagents.

Carry all large acid bottles with both hands, one on the bottom and one on the neck.

Never fill the ether bottle full.

Water should never be poured into concentrated H_2SO_4. Always introduce the acid, gradually and with stirring, into the water.

Any corrosive liquids which may be poured into the sinks should be washed down immediately with running water.

Always weigh out the specified amounts. Do not guess.

Never place material to be weighed directly on the balance pan. Take two pieces of paper of the same size and kind and then place one on each pan. Put the material to be weighed on the left pan, and counterbalance with the proper weights on the right pan or with the rider. Always return the weights to their proper places in the box or block after completion of the weighing.

When weighing liquids, first place the empty receptacle on the balance pan and counterbalance with shots. Then introduce the liquid and counterbalance again with the proper weights.

Care should be exercised in the use of sodium. Do not allow it to stand exposed to the air. Keep water away from it. Never throw sodium into the sinks or crocks but into a receptacle provided for that purpose. Whenever you cut sodium hold it in a filter paper.

Do not handle solid NaOH or KOH with the fingers. These materials are corrosive.

To break a stick of NaOH or KOH place it on a piece of paper. Fold the paper over it and strike with a pestle.

NaOH solutions should be kept in rubber-stoppered bottles. Never use a glass-stoppered bottle for this purpose.

Below is given a table of strengths of the common acids and ammonium hydroxide.

	sp. gr.	Contains	100 cc. contain
Acetic acid, glacial	1.06	99.5% acetic acid	105.6 g. of $CH_3 \cdot COOH$
Hydrochloric acid, conc	1.178–1.183	35–36% HCl	41.23–42.58 g. of HCl
Nitric acid, conc	1.42	70% HNO_3	99.4 g. of HNO_3
Sulfuric acid, conc	1.84	96% H_2SO_4	176.6 g. of H_2SO_4
Ammonia, conc	.90	29% NH_3	26.1 g. of NH_3

The concentrations of solutions are indicated either by percentage, such as 10 per cent, or by ratio, such as 1 : 10. To prepare a 10 per cent solution by volume dissolve 10 g. of the substance in the solvent (water, unless otherwise specified) and make up the total volume to 100 cc. (room temperature). To prepare a 10 per cent solution by weight dissolve 10 g. in 90 g. of solvent. The total weight is 100 g. A 1 : 10 solution can be prepared, in case of solids, by dissolving 1 g. of the solid in 10 cc. of the solvent; in the case of liquids this means 1 cc. of the liquid diluted to a total of 10 cc.

There are approximately, 20 drops of water to 1 cc. from a burette or pipette.

Grades of Purity of Chemicals.

" C. P." (chemically pure) is usually the purest grade obtainable.

" Analyzed " chemicals are those which have the percentages of impurities stated on the label.

" U. S. P." is used in connection with a substance which complies with the requirements of the United States Pharmacopœia as to quality, purity, etc.

" Practical " is a product which, while not of the highest purity, is nevertheless considered suitable for general laboratory work.

" Technical " is the ordinary commercial product. It may be crude, pure, or " C. P."

For the composition of certain reagents (such as Fehling's, Schiff's, etc.) used during the course. see pages 178, 179 of the Appendix.

NOTES ON REPORTS

On the direction sheets the word **"result"** occurs frequently. The space following this word is to be used for recording your observation.

All preparations are to be submitted to the instructor in a proper receptacle; in the case of liquids in a small vial or bottle, in the case of solids in small wide-mouth bottles. These should be stoppered and labeled (in ink) as follows; name of the compound, m.p. or b.p. (as you found it), the yield (in grams), your name and date. Example:—

Aniline
b.p. =
yield = g.
Per cent yield =
John Doe
Date

Save all tests, whenever possible, and submit them to the instructor on completion of the experiment.

In writing answers to the questions on the report sheets, keep the following points in mind:—

(*a*) Use good English.
(*b*) Use graphic formulas wherever possible.
(*c*) Write names under formulas of all organic compounds.
(*d*) When a reaction occurs in steps show all these in writing the equations.
(*e*) (A suggestion). After reading a question, first write the answer on a separate piece of paper and after you have formulated a clear, concise answer, transcribe to the report sheet.

As soon as a report sheet is returned to you, approved, neatly paste it back into its former place using transparent mending tape (which can be bought in rolls) on both sides of the sheet.

Upon the completion of the course tear off the brown paper cover of the book and you have a bound copy of your laboratory directions and reports of experiments.

NOTES RELATING TO FIRES AND ACCIDENTS IN THE LABORATORY

In case of a small fire (such as in a beaker or flask, etc.) first turn off the gas. Then attempt to smother the fire with an asbestos pad or a wet towel. If this fails use the " Pyrene " fire extinguisher or a bottle of carbon tetrachloride provided for this purpose. In case of a larger fire use the fire extinguishers or blanket provided for this purpose. In general, do not use water. This will usually result in scattering the fire. In case of a phosphorus or sodium fire, smother it by throwing sand on it. If your clothing catches fire use the shower arrangement provided for this purpose.

First Aid.—It is recommended in all cases that after first aid treatment, the student should see a physician.

Never use a strong acid or base to neutralize each other on your clothing or body.

Acid in Eye.—Wash thoroughly with running water. Then by means of an eye cup bathe with a 2 per cent sodium bicarbonate solution. Dry with sterile gauze and put several drops of olive oil into the eye.

Alkali in Eye.—Wash thoroughly with running water and then bathe with a saturated solution of boric acid. Dry with sterile gauze and drop olive oil into the eye.

Cuts.—First wash thoroughly with water and then apply 50 per cent alcohol or tincture of iodine. Bandage with sterile gauze. Do not continue to use iodine in subsequent dressings. (Burns will result.) Never cover directly with adhesive tape.

Burns.—*If Acid.*—Wash first with running water and then with a saturated sodium bicarbonate solution. Cover for about ten minutes with solid sodium bicarbonate. Wash off, and dry with sterile gauze and apply carron oil (an equal mixture of lime-water and linseed oil). Always shake this mixture before using.

If Alkali.—Wash first with running water and then with saturated boric acid solution. Cover for about 10 minutes with powdered boric acid. Wash off, dry with sterile gauze and apply carbolated vaseline.

In Case of **heat burns.**—Apply carron oil or carbolated vaseline or butesin picrate.

After application of carron oil or carbolated vaseline in the above cases, cover with a light bandage.

In Case of a **Bromine Burn.**—Wash with running water and treat at once with a concentrated solution of sodium thiosulfate until all the bromine has been removed. Wash thoroughly, dry and then apply carron oil or vaseline.

Bromine or Chlorine Poisoning is best treated by the inhalation of alcohol or aromatic spirits of ammonia. Remove patient to open air.

In Case of **Phenol Burns.**—Wash thoroughly with 50 per cent alcohol until all traces of phenol are washed off. Dry and apply vaseline or carron oil.

In Case of Fainting.—Lay patient flat on his back with his head low. Open clothes, rub limbs towards heart. After sign of motion administer at once aromatic spirits of ammonia (½–1 cc. in 100 cc. of water).

Report all cases of accidents to the instructor in charge.

Familiarize yourself with locations of the first-aid cabinet, fire extinguishers, blankets, shower arrangement, and exits.

GENERAL SOLUBILITIES OF CLASSES OF ORGANIC COMPOUNDS

General Rule.—A solvent dissolves those compounds which are chemically closely allied to it.

Hydrocarbons and their halogen substitution products are either insoluble or only very slightly soluble in water. They dissolve in alcohol, ether, benzene, etc.

The solubility of a compound in water increases with the increase of oxygen content; especially is this true when the oxygen atoms are combined with hydrogen as in $-OH$ groups.

The homologues of low molecular weight of the aliphatic series, such as alcohols, aldehydes, ketones, amines, and acids, are soluble in water; but the solubilities decrease with increasing molecular weight.

Alkali salts of acids, salts of amines, sugars, polybasic acids, hydroxy acids, sulfonic acids, and polyhydroxy alcohols are soluble in water.

Esters are very slightly soluble in water, but soluble in alcohol and ether.

Ether dissolves very many organic compounds. (Not salts of acids.) It is slightly soluble in water and is used for extracting products from aqueous solutions.

Acid anhydrides are soluble in alcohol and ether.

Fats and oils are insoluble in water, but readily soluble in benzene, ether, chloroform, etc.

Nitro compounds are insoluble in water but soluble in alcohol and ether.

The presence of a sulfonic acid group increases the solubility of an organic compound in water.

The hydroxy derivatives of aromatic hydrocarbons are soluble in water, but more so in alcohol and ether.

The *p*-compounds are less soluble in the various solvents than the isomeric *o*- and *m*- compounds.

Alkaloids are usually insoluble in water, but soluble in alcohol, chloroform, benzene, etc.

Homologues are mutually soluble.

RULES FOR DRYING

A considerable amount of the moisture adhering to solids may be removed by pressing between filter papers. More can be removed by spreading in a thin layer and pressing the substance on a porous plate. Desiccators or heating ovens are generally used for complete drying. Liquids are usually dried by adding a solid which will combine with the water. The drying agent should have no action upon the organic compound. Some common drying agents are anhydrous $CaCl_2$, anhydrous K_2CO_3, anhydrous Na_2SO_4, CaO, KOH, and NaOH. If enough water is present to form two layers, it is first removed by using a separatory funnel of suitable size. To remove the moisture which may be absorbed or dissolved by the liquid a drying agent is added. Agitate often and allow to stand for some time. The liquid is poured off from the drying agent and distilled. The use of excessive amount of drying agents should be avoided.

For drying alcohols and bases do not use $CaCl_2$. For drying acids, phenols, alcohols, esters do not use NaOH or KOH.

In addition to the above mentioned drying agents, the following are also used:—Al_2O_3, H_2SO_4, MgO, $CuSO_4$, $ZnCl_2$, etc.

Approved by

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EXPT. 1. METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

< An organic compound resulting from a reaction is usually impure, owing to the presence of small amounts of the materials from which it was prepared or to by-products or other products formed by secondary reactions. These impurities may either be mixed with the compound or adsorbed by it. (~~Where~~ver possible pure substances should be employed in all experimenta~~l work~~.) Therefore it becomes necessary to eliminate the impurities. A few of the general methods used for this purpose are outlined below. The method to be used in any one case will depend upon the nature of the substance to be purified and also upon the impurities present.>

Methods.—For discussion of theories and additional methods of manipulation, refer to Gattermann and Wieland " Laboratory Methods of Organic Chemistry." (General Part.)

(*a*) **Crystallization.**—1. Place 7 g. of crude oxalic acid in a 50 cc. beaker. Add 25 cc. of water, boil for 2 minutes, filter hot and set the filtrate aside to cool. **Result:**—

2. In a test tube dissolve 2 g. of urea in 10 cc. of alcohol by heating in a water bath and stir until all the urea is dissolved. Set aside to cool. **Result:**—

3. Crystallization at low temperature (freezing): Place 10 cc. of pure benzene in a test tube and place in a freezing mixture (ice and salt). Allow to stand for a few minutes, stir and examine. **Result:**—

Choice of Solvent for Recrystallization.—When purifying compounds use a solvent in which the compound is only slightly soluble at ordinary temperatures, but in which its solubility increases as rapidly as possible with the temperature. At the same time choose the solvent in which the impurities which may be present will be as soluble as possible at the low temperatures.

(*b*) **Distillation.**—Add 25 cc. of acetone to 10 cc. of water. Pour this mixture into a 100 cc. distilling flask. Arrange the apparatus as shown in Fig. 8 and distill. Note that most of the acetone distills at 56° and at the end the water distills at approximately 100°.

(*c*) **Extraction.**—Pour 50 cc. of a saturated solution of picric acid into a small separatory funnel and shake with 20 cc. of ether. Allow to stand until the two layers separate. The upper layer contains the ether solution. Draw off the lower layer into a small beaker. Draw off the ether layer into a small evaporating dish. Pour the aqueous solution back into the separatory funnel and repeat the extraction with an additional 10 cc. of ether. Separate the layers as before. Combine the two ether extracts and allow to evaporate in the hood. **Result:**—

NOTE.—*Since ether is very flammable, have no flames within a radius of* 10 *feet.*

(*d*) **Sublimation.**—Place a quarter of a moth ball (naphthalene) in a dry test tube. Hold the tube in an inclined position and heat. Observe the sublimate on the side of the test tube. **Result:**—

(*e*) **Dialysis.**—Make a starch suspension by stirring 1 g. of starch with 20 cc. of distilled water. Pour this into 100 cc. of boiling distilled water. Stir and boil for about 2 minutes and then cool. Break the closed end of a test tube by dropping a file into it. Now heat in the flame until the edges are rounded and a fairly large opening is formed. Tie a piece of parchment paper around the rim of the other end so as to form a large tightly sealed bag. Mix 50 cc. of the starch solution with 20 cc. of a 10 per cent solution of NaCl in distilled water. Through a funnel pour enough of this mixture into the bag to fill it to three-quarters of its capacity and place the bag in a beaker of distilled water so that the liquid in the beaker and that in the bag are at the same level. Set aside until the next laboratory period. Then test the dialysate (liquid in the beaker) both for starch and NaCl. Test for starch by adding a few drops of a solution of iodine in potassium iodide to 5 cc. of the liquid; a blue color would indicate the presence of starch. **Result:**—

Test for NaCl by adding a few drops of 10 per cent $AgNO_3$ solution to 5 cc. of the liquid. **Result:**—

(*f*) **Decolorization.**—Dissolve 10 g. of brown sugar in 35 cc. of water. Filter. Save 10 cc. of the filtrate for comparison. To the remainder add about 3 g. of bone-black and gently boil for 15 minutes. Filter and compare the color of this solution with the original. **Result:—**

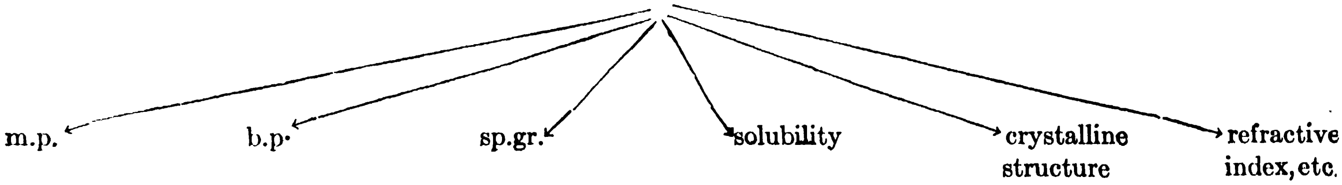
(*g*) **Formation of Addition Compounds.** —Experiments illustrating this method will be conducted with acetone. Expt. (*i*) (p. 72), and naphthalene Expt. (*d*) (p. 159).

IMPURE ORGANIC COMPOUNDS

Methods of Purification.—

- (*a*) Distillation
  - Fractional
  - Under reduced pressure (to prevent decomposition)
  - Steam
  - Superheated steam
- (*b*) Extraction with
  - Ether
  - Benzene
  - Chloroform, etc.
- (*c*) Crystallization
  - By evaporation
  - With two miscible solvents
  - At low temperatures
    - *Solvents*
    - water
    - ethyl alcohol
    - ether
    - acetic acid
    - benzene
    - carbon disulfide
    - acetone
    - chloroform
    - toluene
    - aniline
    - methanol, etc.
- (*d*) Sublimation
- (*e*) Dialysis
- (*f*) Addition compounds and subsequent decomposition.
- (*g*) Decolorization.
- (*h*) Precipitation,

PURE COMPOUNDS (Identified by)



Approved by. . . . . *Name*. . . . .

Section. . . . . *Date*. . . . .

EXPT. 1. METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

1. Why is it necessary to purify organic compounds?

2. List the general methods for purifying organic compounds.

3. What general solubility law is illustrated in Expt. (*a*) 1 and (*a*) 2?

4. Explain the principle of crystallization as illustrated in Expt. (*a*).

5. Explain the principle of distillation as illustrated in Expt. (*b*).

6. Explain the principle of extraction as illustrated in Expt. (*c*). What law applies?

7. Explain the principle of sublimation as illustrated in Expt. (*d*).

8. Explain the principle of dialysis as illustrated in Expt. (*e*).

9. Explain the principle of decolorization as illustrated in Expt. (*f*).

Approved by

..Ahmed K. [illegible]......

EXPT. 2. DETECTION OF THOSE ELEMENTS OCCURRING MOST FREQUENTLY IN ORGANIC SUBSTANCES

(Pure compounds should be used for these tests. Also use distilled water.)

(*a*) **Tests for Carbon.**—1. Charring of organic substances: Place about $\frac{1}{4}$ g. of sugar ($C_{12}H_{22}O_{11}$) on a crucible lid and heat. The charring indicates the presence of carbon. Heat strongly until no black particles remain. What remains on the crucible lid?

2. Non-charring of organic substances: (i) Place 1 g. of naphthalene ($C_{10}H_8$) in a crucible with a cover With a very small flame *gently* heat only the bottom of the crucible for a minute. Allow to cool, and examine the underside of the crucible cover. **Result:**

(ii) Place 2 cc. of ethyl alcohol (C_2H_5OH) on a crucible lid and heat. **Result:**—

(*b*) **Test for Carbon and Hydrogen.**—Heat about 5 g. of powdered cupric oxide to red heat in an open crucible to expel moisture. Cover and allow to cool. Grind half of it thoroughly with about $\frac{1}{2}$ g. of sugar. Place this mixture in a 20 cm. hard-glass test tube, pour the remainder of the copper oxide on top of the mixture (arrange the apparatus as shown in Fig. 1) and heat gradually, beginning at the front end. Examine the side of the tube near the open end and also note the effect in the lime-water.

Result:—

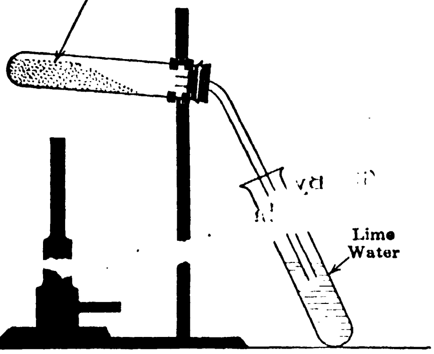


Fig. 1.

Note.—*Be sure to remove the end of the delivery tube from the lime-water before the flame is removed.* **Why?**

(*c*) **Test for Oxygen.**—There is no satisfactory qualitative or quantitative test for oxygen.

(*d*) **Tests for Nitrogen.**—1. Decomposition with soda-lime ($NaOH + CaO$): Grind together in a mortar $\frac{1}{2}$ g. of albumin and 5 g. of soda-lime. Place in a test tube and heat. Test the vapors with moistened red litmus paper. **Result:**—

Note.—In this test a negative result does not necessarily indicate the absence of nitrogen, for certain types of compounds do not respond to this test.

2. Decomposition with sodium (Lassaigne's method): Clamp a clean dry test tube in a vertical position and drop into it a small piece (about the size of a pea) of freshly cut sodium which has been thoroughly dried with filter paper.* Heat the tube until the sodium has melted and started to vaporize. Then introduce by means of a spatula a very small amount of finely pulverized urea (CON_2H_4), being careful to drop the material directly on the melted sodium.. Add a second portion of the urea and continue heating for a minute. Allow the tube to cool. Place it in a mortar containing 3 cc. of alcohol and break the end of the tube with a pestle. When the evolution of gas has ceased add 15 cc. of distilled water. Transfer the contents from the mortar to a small beaker and boil for a few minutes. Filter. To the filtrate add a few drops of 10 per cent NaOH solution, 1 cc. of 10 per cent ferrous sulfate solution and 1 drop of ferric chloride solution; boil for a minute; cool with running water and carefully add a 10 per cent solution of HCl until

the precipitate of ferrous hydroxide has just dissolved. A precipitate or a deep blue or bluish-green coloration of Prussian blue should form.

$$\underset{\text{Organic compound}}{\mathrm{Na + C + N}} \rightarrow \mathrm{NaCN}$$

$$2NaCN + FeCl_2 \rightarrow Fe(CN)_2 + 2NaCl$$

$$Fe(CN)_2 + 4NaCN \rightarrow Na_4Fe(CN)_6$$

$$3Na_4Fe(CN)_6 + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl.$$

(*e*) **Test for Halogen.**—1. Beilstein Test: Make a small loop at the end of a copper wire and heat in a non-luminous flame until no more color is imparted to the flame. Allow to cool, dip into a drop of chloroform ($CHCl_3$) and hold in the flame. **Result:**—

2. Lime method: Grind together 5 g. of quicklime (CaO) (halogen-free) and 1 g. of dichlorobenzene ($C_6H_4Cl_2$). Place the mixture in a test tube and gradually bring to red heat. Allow the tube to cool, dissolve the contents of the tube in 10 per cent nitric acid and filter. The solution must be acid. Add a few drops of 10 per cent $AgNO_3$ solution. **Result:**—

3. Decomposition with sodium: Repeat Expt. (*d*)2 with a few crystals of iodoform (CHI_3) instead of urea. Acidify the filtrate after solution in water with 10 per cent HNO_3 (testing with litmus paper) and add $AgNO_3$ (10 per cent solution). **Result:**—

(*f*) **Test for Sulfur.**—1. Alkali test: Boil for a period of 30 minutes about ½ g. of powdered egg albumin with 10 cc. of 50 per cent NaOH solution. Periodically replace the water as it boils off, *adding 2 or 3 drops* at a time. This solution may be tested for the sulfur content by any of the three following methods:

(i) By placing a drop of the solution on a silver coin. A brownish-black stain of silver sulfide is produced.

[illegible] By acidifying with dilute acetic acid and then adding a few drops of 10 per cent lead acetate solution [illegible] brownish-black precipitate of lead sulfide is produced.

(iii) By [illegible] cc. of the alkali solution with 100 cc. of water and adding a few drops of sodium nitroprusside solution, a violet color is produced on standing.

2. Decomposition with sodium: Repeat Expt. (*d*)2 with a few crystals of thiocarbanilide instead of urea. After being dissolved in water put a few drops of the filtrate on a silver coin. **Result:**—

(*g*) **Test for Phosphorus.**—Fusion with KNO_3, Na_2CO_3 mixture: Thoroughly mix 1 g. of KNO_3, 2 g. of Na_2CO_3, and 0.3 g. of powdered egg albumin. Place the mixture in a porcelain crucible and heat cautiously at first on an asbestos pad and then more strongly on a triangle until no more charred matter remains. Stir with a glass rod during the fusion. Allow to cool; boil the mixture with 10 cc. of water and filter. Just acidify the filtrate with HNO_3, and then add 5 cc. of ammonium molybdate solution (10 per cent) and warm to 65°. A yellow precipitate of ammonium phosphomolybdate, which indicates the presence of phosphorus, forms on standing.

$$\underset{\text{Fusion}}{Na_2CO_3} + \underset{\text{Oxidizing agent}}{KNO_3} + \underset{\text{Organic compound}}{P} \rightarrow Na_3PO_4$$

$$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O.$$

(*h*) **Test for Metals.**—Place 1 g. of sodium acetate in a crucible and heat strongly. The residue is Na_2CO_3. Allow to cool, and add (10 per cent) HCl to the residue. **Result:**—

NOTE.—*Metallic elements in organic compounds are generally converted upon ignition into their respective oxides, carbonates, sulfates, etc.*

After completion of the above experiments the instructor should provide each student with two or more unknown compounds and have the elements present in each determined and reported.

Record the results of the unknown samples.

Approved by............................... *Name*.......... ....

Section................*Date*................

EXPT. 2. ELEMENTS OCCURRING IN ORGANIC SUBSTANCES

1. Why is it necessary to conduct these tests on absolutely pure compounds?

2. What are the elements most frequently present in organic compounds?

3. Do all organic compounds char when heated? Name exceptions. What happens if they do not char?

4. If an organic compound contains C, H and O as in sugar, what are its oxidation products?

5. What are the reddish particles remaining in the test tube in Expt. (*b*)? How do you account for their presence?

6. Into what compound is the nitrogen converted in Expt. (*d*)1?

7. Outline a method to detect the presence of halogen, sulfur and nitrogen in an organic compound by the sodium fusion method.

8. What produces the green color in the flame in Expt. (*e*)1?

9. Why must the quicklime in Expt. (*e*)2 be halogen-free?

10. What calcium compound is produced as a result of strong heating in Expt. (*e*)2?

11. What sulfur compound is formed in Expt. (*f*)1?

12. Explain the use of the KNO_3 and Na_2CO_3 in the fusion mixture in Expt. (*g*).

13. Why is distilled water used in making these qualitative tests?

14. By what physical constants can you determine the purity of an organic compound?

15. If an organic compound containing C, H, O, N, X, S, P, is fused with metallic sodium, what sodium compounds would be formed?

16. What method is used to dispose of unused sodium?

EXPT. 5. FRACTIONAL DISTILLATION

Fractional distillation is a method employed to separate a mixture of two or more liquids into its components. It is generally conducted in an apparatus such as that shown in Fig. 8. It is often a very tedious process, but a great amount of time and expense can be saved by the use of efficient still-heads or distillation columns. (Fig. 11.)

If a mixture of two substances is distilled, the first part of the distillate is richer in the more volatile component than the residue. A mixture of two miscible liquids, such as toluene and benzene, has a definite vapor pressure depending on the temperature and the composition of the mixture. In the vapor above the liquid there are found both kinds of molecules, each of which contributes a part to the total pressure. If the composition of the vapor is determined, it is usually found that the more volatile constituent is present in greater proportion than in the liquid. For example, a liquid consisting of about 50 per cent toluene and 50 per cent benzene gives off a vapor in which there is about 70 per cent benzene and 30 per cent toluene. Therefore, if this original liquid is boiled and the vapor condensed, the distillate will be richer in benzene than the original solution. If this distillate is in turn boiled and the resulting vapor condensed, there will be collected a new distillate containing a still larger percentage of benzene than before. The more frequently this process is repeated the larger will be the percentage of benzene in the final distillate. In many cases one constituent can thus be completely separated from the other.

In general, the farther apart the boiling points the easier is the separation. There should be a difference of at least 25°–35° in boiling points of the liquids to be separated. Often two or more liquids form constant boiling-point mixtures. This method of separation cannot be applied to such a mixture. Thus a mixture of 95.5 per cent by weight of ethyl alcohol and 4.5 per cent of water cannot be separated by distillation. The water must be removed by chemical means if absolute alcohol is desired. (See p. 55.)

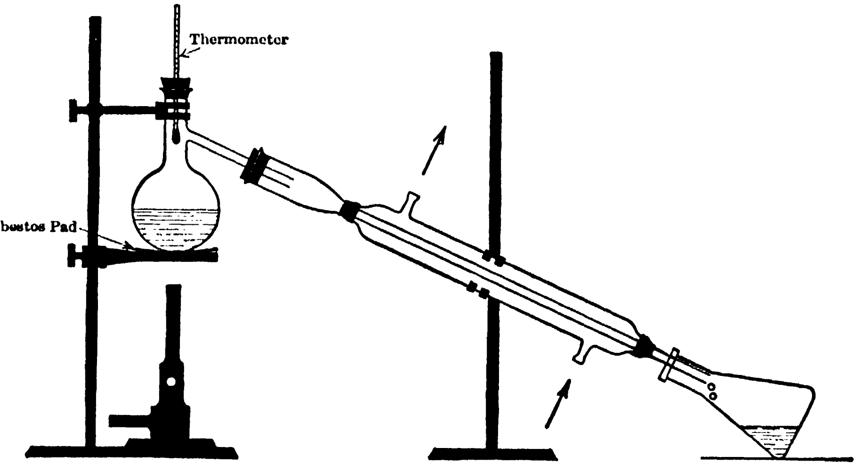


FIG. 8.

(*a*) **Fractional Distillation of a Mixture of Ethyl Alcohol and Water.**—Mix together in a 200 cc. distilling flask 50 cc. of ethyl alcohol and 50 cc. of distilled water. (Pour the liquids into the distilling flask through a long-stem funnel.) Arrange the apparatus as in Fig. 8 and heat. It is essential that the distillation take place slowly and uniformly, otherwise erroneous results will be obtained. The distillation should proceed at such a rate that not more than 30 drops of distillate per minute are collected in the receiving flask. Fractions are to be collected between the following temperature limits: 78°–82°, 82°–88°, 88°–95°, and 95°–100°. Place labels with these temperature limits on four 50 cc. Erlenmeyer flasks or bottles. These are to be used as receivers. As soon as the upper temperature limit of each of the above-mentioned fractions is reached, remove the receiver, and immediately replace it with the flask next in order. Immediately stopper the flasks containing the collected fractions. Now measure the volumes of the collected fractions.

Record these volumes in the table given below. Now repeat the distillation process, first placing in the distilling flask the fraction collected between 78°–82°, placing the emptied Erlenmeyer flask at the end of the condenser. When the 82° mark is reached, allow the contents of the distilling flask to cool slightly, and then add the fraction collected between 82°–88°. Heat and collect any liquid distilling below 82° in the 78°–82° flask. As soon as the 82° mark is reached remove the 78°–82° receiver, replacing it by the 82°–88° receiver. As soon as the 88° mark is reached, allow the distilling flask to cool slightly, and then add the contents of the 88°–95° receiver, collecting in the 82°–88° receiver any liquid distilling over below 88°. As soon as the 88° mark is reached replace the 82°–88° receiver by the 88°–95° receiver. When the temperature reaches 95°, allow the distilling flask to cool slightly. Add the contents of the 95°–100° receiver, collecting in the 85°–95° receiver any liquid distilling over below 95°. Now collect the fraction distilling between 95°–100° in the 95°–100° receiver. Record your results. Make a third distillation, following the principle and steps used in the second distillation, and record the results.

The closer the temperature limits of each fraction and the greater the number of distillations the greater the degree of separation of the compounds.

Distillation No.	78°–82°	82°–88°	88°–95°	95°–100°	Total
1	—— cc.	—— cc.	—— cc.	—— cc.	—— cc.
2	—— cc.	—— cc.	—— cc.	—— cc.	—— cc.
3	—— cc.	—— cc.	—— cc.	—— cc.	—— cc.

Note that the first fraction (78°–82°) and the last fraction (95°–100°) increase in amount with subsequent distillations while the intermediate fractions decrease in amount.

For further details on the principle of fractional distillation see Sidney Young's book on "Distillation Principles and Processes" and Robinson on "The Elements of Fractional Distillation."

While the class is conducting the experiment on fractional distillation the following demonstration can be given:*

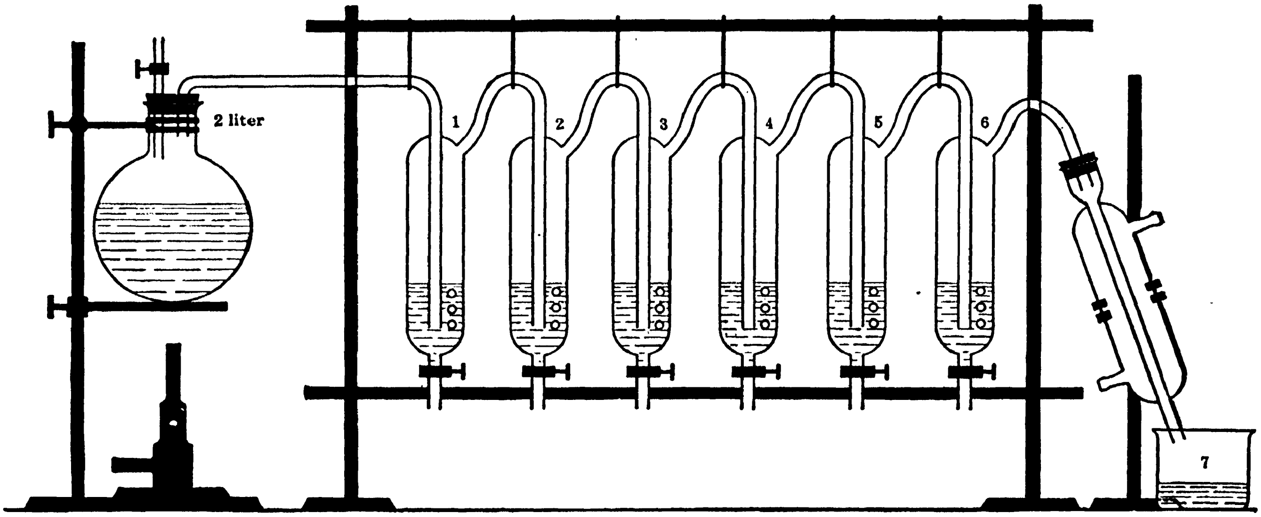


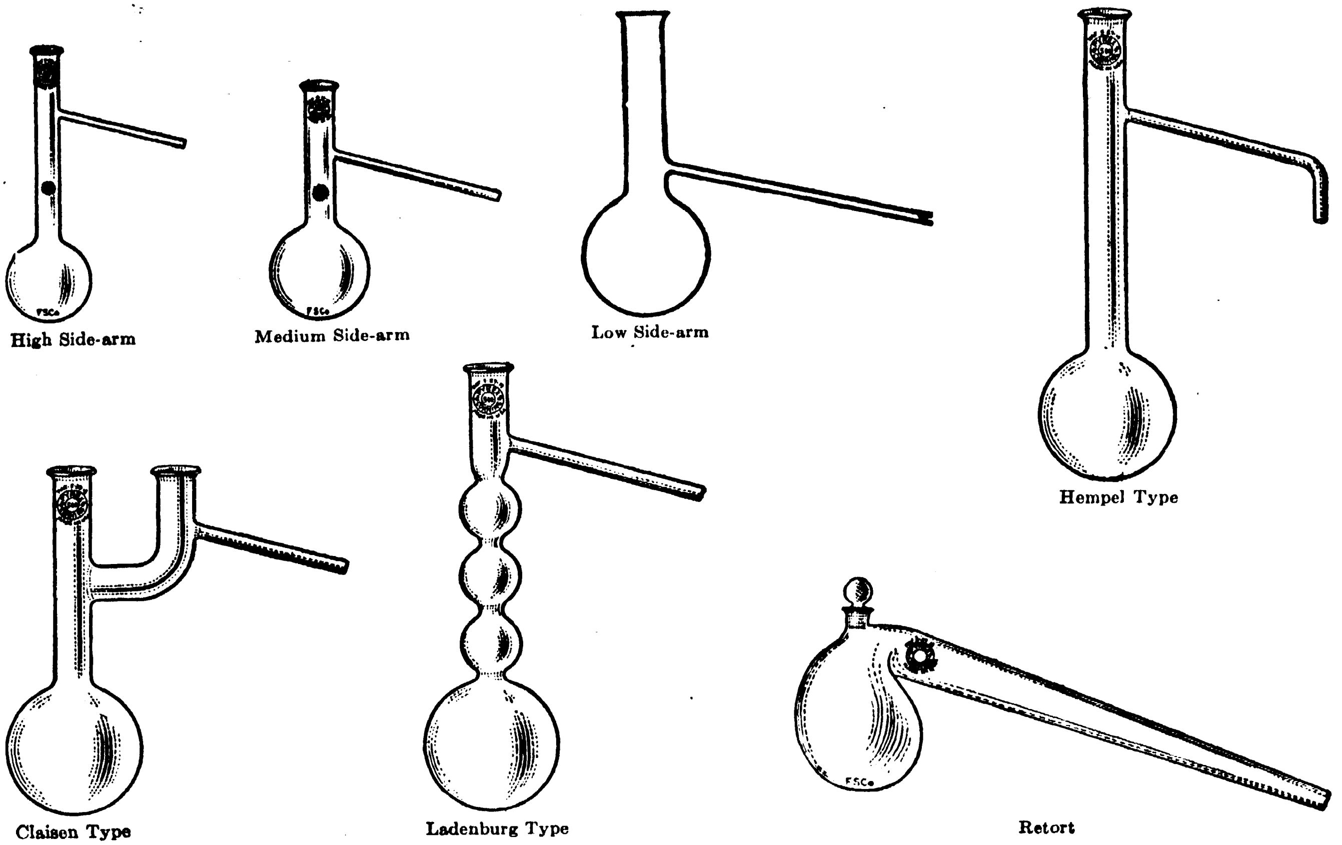
Fig. 9.

Set up the apparatus as shown in Fig. 9. Pour a mixture of 200 cc. of alcohol and 1400 cc. of water into a 2-l. flask. Boil slowly. Endeavor to have sufficient condensate in the first vessel to cause "bubbling effect" before there is condensation in the second vessel. When 25–30 cc. of the mixtures have been collected in each vessel drain the contents into small graduates. Cool to either 15° or 20° and take accurate hydrometer readings of each. By referring to alcoholometric tables, indicate the percentages present in each vessel.

1 = = per cent alcohol + per cent water.
2 = = per cent alcohol + per cent water.
3 = = per cent alcohol + per cent water.
4 = = per cent alcohol + per cent water.
5 = = per cent alcohol + per cent water.
6 = = per cent alcohol + per cent water.
7 = = per cent alcohol + per cent water.

Young—Ind. and Eng. Chem., 17, 984 (1925)—Apparatus sold by Fisher Scientific Co., Pittsburgh, Pa.

Equipment for Distillation



High Side-arm

Medium Side-arm

Low Side-arm

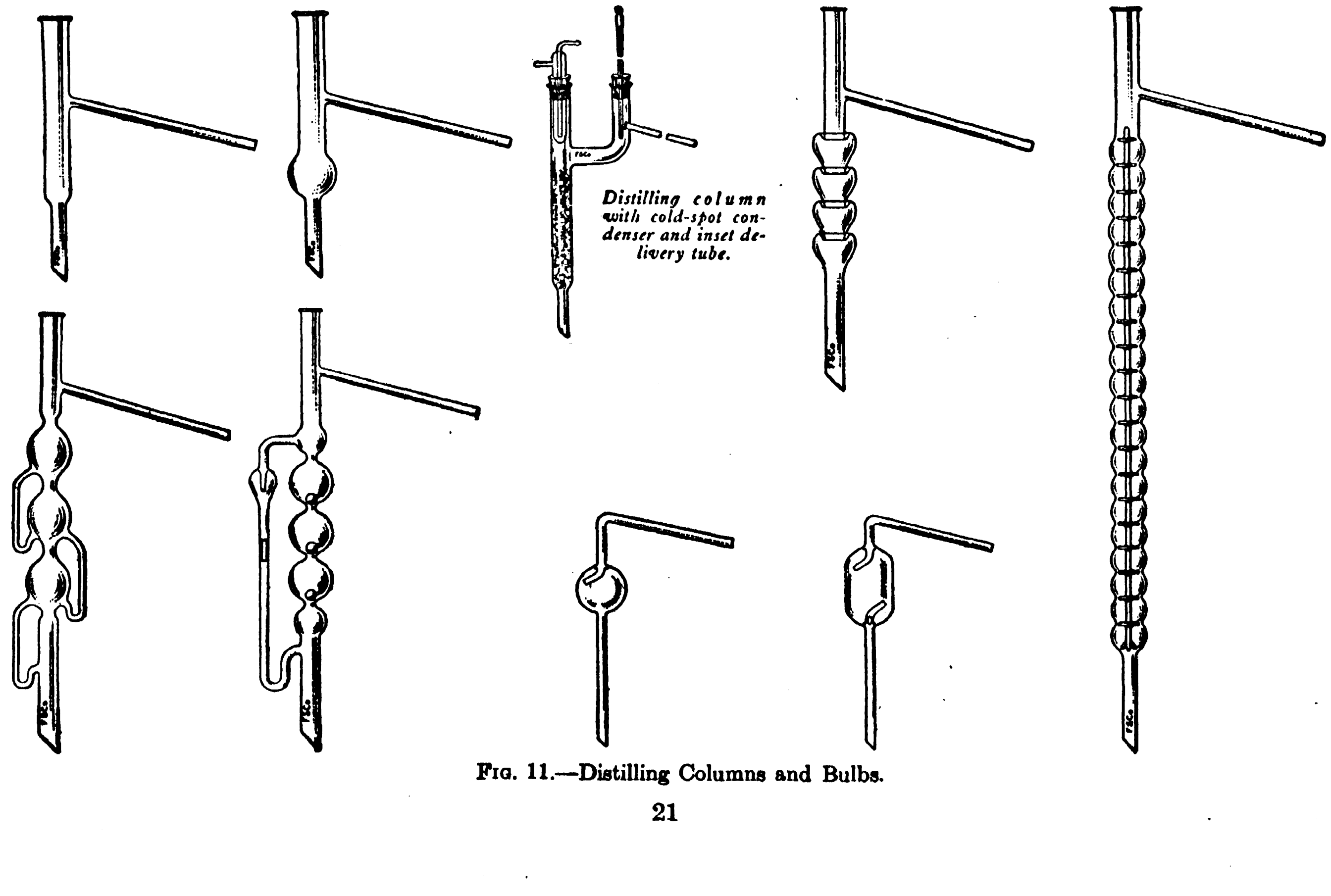
Hempel Type

Claisen Type

Ladenburg Type

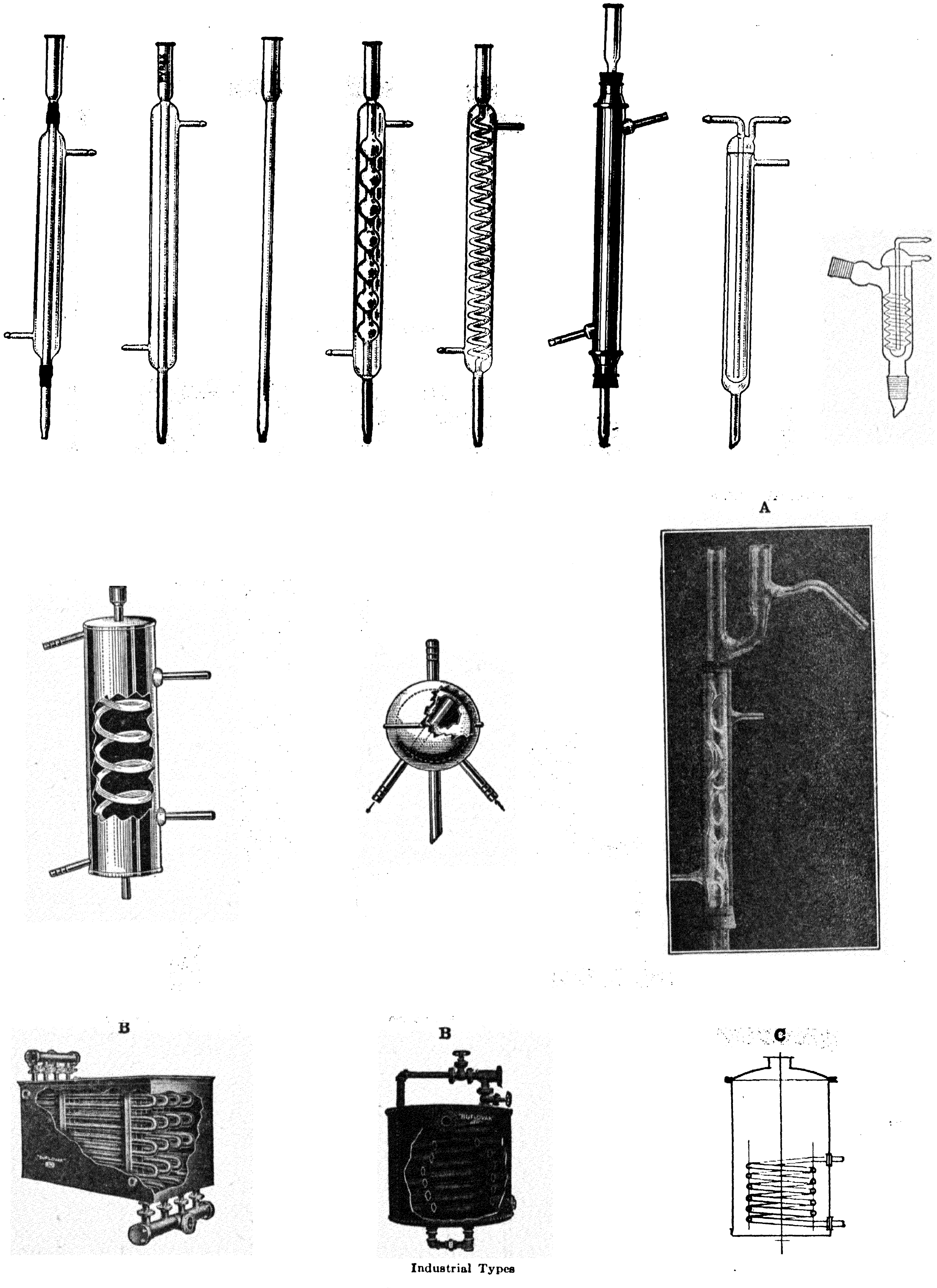
Retort

Fig. 10.—Flasks and Retort.



Distilling column with cold-spot condenser and inset delivery tube.

Fig. 11.—Distilling Columns and Bulbs.



Industrial Types

FIG. 12.—Condensers.

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EXPT. 5. FRACTIONAL DISTILLATION

1. Explain the principle involved in fractional distillation.

2. Mention different types of mixtures for which the fractional distillation method of separating components is not possible.

3. Would you be able to separate a mixture of water and sugar by this method? Give your reason.

4. Why is distillation conducted at a slow rate in this experiment?

5. The total volume at the end of each distillation is not 100 cc. Why?

6. What results in your table indicate the fact that you are separating the components?

7. What are the advantages of distilling or fractionating columns shown in Fig. 11?

8. What should be the exact position of your thermometer in the distilling flask during the distillation?

9. What is the advantage in using an asbestos pad in this experiment instead of a wire gauze?

10. Where is the proper place to clamp (*a*) a distilling flask, (*b*) condenser?

11. What is the advantage of the Ladenburg type of distilling flask shown in Fig. 10 over the plain types?

12. Where is the thermometer placed in the Claisen type flask shown in Fig. 10?

13. What advantage do the coil and bulb types of condensers have over the straight tube (Liebig) types shown in Fig. 12?

14. When would you use a retort (Fig. 10) in preference to a distilling flask?

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PREPARATION OF A PARAFFIN HYDROCARBON

EXPT. 6. METHANE

Preparation.

Thoroughly grind together in a mortar 20 g. of soda-lime ($NaOH+CaO$) and 12 g. of freshly fused sodium acetate * (CH_3COONa). Place the mixture in a 20 cm. test tube (hard glass). Tap the tube in order to leave an air space above the mixture. Set up the apparatus as shown in Fig. 13. Use a rubber stopper.

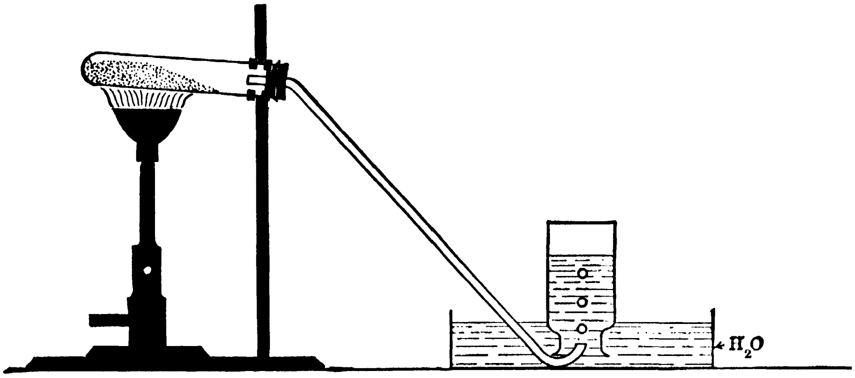


FIG. 13.

Heat the tube, keeping the flame in motion. *Do not remove the flame until the required amount of gas has been collected.* Rapid evolution of gas at the beginning indicates the displacement of most of the air in the apparatus. Collect 4 bottles of the gas by displacement of water. Fill the fifth bottle to exactly one-tenth of its capacity with water and displace this volume with methane. Until the properties of the gas are studied, keep the bottles in the trough or in an inverted position covered with glass plates. After the required amount of methane has been collected lift the delivery tube from the water and light the issuing gas. Burn the gas for a minute and remove the flame from the test tube.

Properties.

(*a*) **Explosive Mixture of Methane and Air.**—The fifth bottle mentioned above contains approximately nine-tenths of air and one-tenth of methane by volume. Lift the cover and ignite the mixture. **Result:**—

(*b*) **Flammability and Products of Combustion.**—Ignite a bottle of the gas collected, and after burning add 15 cc. of lime-water. Shake. **Result:**—

(*c*) **Action of Bromine on Methane.**—To another bottle of the gas add 5 cc. of bromine water. Cover and shake until the color just disappears. (Do not invert the bottle.)

Immediately blow across the mouth of the bottle. **Result:**—

Immediately hold a piece of moist blue litmus paper in the mouth of the bottle. **Result:**—

---

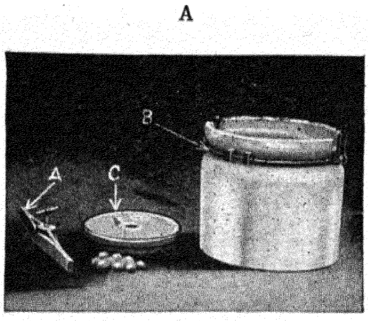
* The fused sodium acetate may be prepared by heating the hydrated sodium acetate with continuous stirring in an evaporating dish. It first melts, then becomes solid, and finally fuses to a transparent mass. Care must be taken not to heat too strongly, for the acetate decomposes at high temperatures. This is shown by the charring of the substance and the evolution of combustible gases.

(*d*) **Methane and $KMnO_4$.**—To another bottle of the gas add 3 cc. of a $KMnO_4$ solution (0.01 per cent). Cover and shake. **Result:—**

If a slight decolorization takes place it is due to impurities distilled over with the methane.

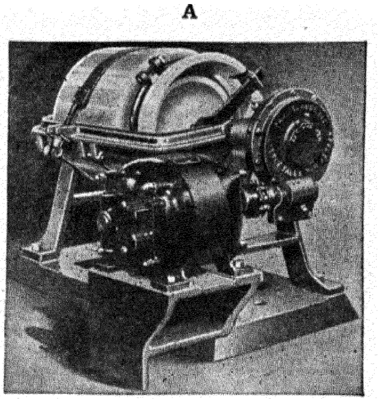
(*e*) **Identification of the Product Left after Distillation.**—To the residue in the test tube used in the preparation of methane add dilute HCl (1 : 4). **Result:—**

NOTE.—NaOH, H_2SO_4, and HNO_3 have no effect on methane.

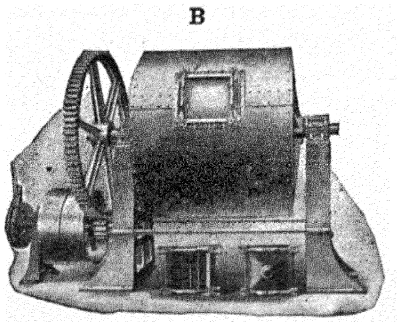


Parts of a Ball Mill

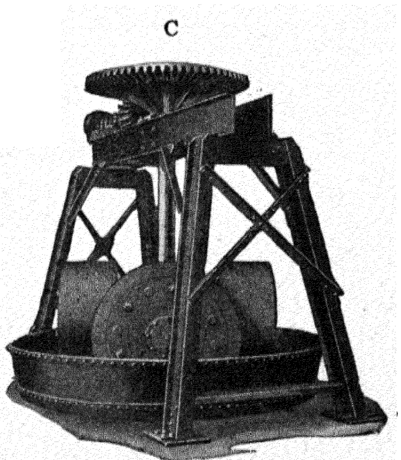
A—Crossbar for holding the cover in place.
B—Neckband with loops for Crossbar ends.
C—Rubber gasket fitted around the cover.



Ball Mill



Pebble Mill



Masticator

FIG. 14.—Grinding Machinery.

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EXPT. 6. METHANE

1. Write the equation for the preparation of methane.

2. Write the type equation for the preparation of saturated hydrocarbons by this method.

3. Why is soda-lime used in place of sodium hydroxide.

4. Why is an air space left above the mixture of sodium acetate and soda-lime?

5. Why keep the bottles containing the methane in an inverted position?

6. Why is the flame not removed from the test tube while you are collecting the gas?

7. Write the equation for the reaction in Expt. (*a*).

8. Why is the ratio of 9 to 1 used in Expt. (*a*) to obtain an explosive mixture? Show this by calcula

9. Write the equations for the reactions in Expt. (*b*).

10. Write the equation for the reaction in Expt. (*c*).

11. What is the general name for the type of reaction illustrated in Expt. (*c*)?

12. What compound caused the change in color of the litmus paper in Expt. (*c*)?

13. List the physical properties of methane which you have observed.

14. What is the compound with which the acid reacts to produce the effervescence in Expt. (*e*)? Give equation.

15. Discuss the occurrence and uses of methane.

16. Give equations for several general methods for the preparation of paraffin hydrocarbons.

17. Summarize the chemical properties of the paraffin hydrocarbons.

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EXPT. 7. FRACTIONAL DISTILLATION OF PETROLEUM

(Laboratory Evaluation Method)

Arrange the apparatus as shown in Fig. 8. Use a cork stopper. Use a 200 cc. distilling flask with a low side-arm, a 360° thermometer, and an adapter at the end of the condenser. By means of copper wire fasten a piece of thin asbestos paper around the neck of the distilling flask. Mount the apparatus to a sufficient height to permit a 100 cc. graduate to be placed under the adapter. Use 100 cc. of crude oil in the distilling flask. Add 4 small pieces of unglazed porcelain to prevent "bumping." Slowly heat the flask on an asbestos pad, regulating the heating so as to prevent excessive frothing. Note the temperature at which the first drop of the condensate falls from the adapter. This is called the "initial boiling point." Continue heating and record the volume of the condensate collected up to the temperatures of 50°, 75°, 100°, 125° and 150°. When the temperature has reached 150°, remove the burner momentarily, allowing the thermometer to drop 5°–10°, and again bring the temperature carefully up to 150°. This is done to distill over any portions which may not have properly distilled on the first rise to 150°. The portion collected up to 150° represents the gasoline and part of the naphtha. At this point remove the flame, turn off the water and drain the condenser, thus converting it into an air-cooled condenser. Replace the receiver by a second graduate for collecting the second fraction. Replace the asbestos pad by a wire gauze. Resume the heating, adding any condensate coming over before 150° to that already collected. With some crude oils it will be possible to reach 300° by this method of distillation; with others the distillation must be discontinued before reaching this temperature. Record the volume of distillate as each 25° interval beyond 150° is passed, ending the distillation when further vapors come over only with difficulty and excessive heating. The fraction collected from 150° up to the end of the distillation contains naphtha, kerosene, fuel oil, and possibly lighter lubricating oils.

When the flask has partly cooled, measure the viscous residue remaining in the flask by pouring it into a graduate. This residue contains lubricating oils, paraffin wax (and asphaltic residuum if the oil is of asphalt base). In refinery practice this residue is distilled with steam (see p. 45) or under a reduced pressure (partial vacuum) (see p. 170).

Results

Volume at the start =		Initial boiling point=
Up to 50° =	cc.	Gasoline and naphtha
50°–75° =	cc.	
75°–100° =	cc.	
100°–125° =	cc.	
125°–150° =	cc.	
150°–175° =	cc.	Kerosene, fuel oil, etc.
175°–200° =	cc.	
200°–225° =	cc.	
225°–250° =	cc.	
250°–275° =	cc.	
275°–300° =	cc.	
Total collected =	cc.	
Residue =	cc.	

(*a*) **Effect of Alkali on Crude Gasoline.**—Treat 10 cc. of the gasoline collected with 5 cc. of NaOH solution (10 per cent) and shake. **Result:**

(*b*) **Effect of H_2SO_4 on Crude Gasoline and Kerosene.**—Treat 10 cc. of the gasoline as collected with 5 cc. of H_2SO_4 and shake. **Result:**—

Repeat with 10 cc. of the kerosene fraction. Note the change in color and odor.

(*c*) **Volatility.**—Pour 1 cc. of the gasoline fraction and 1 cc. of the kerosene fraction on separate small watch glasses. Wave a lighted match over both. **Result:**—

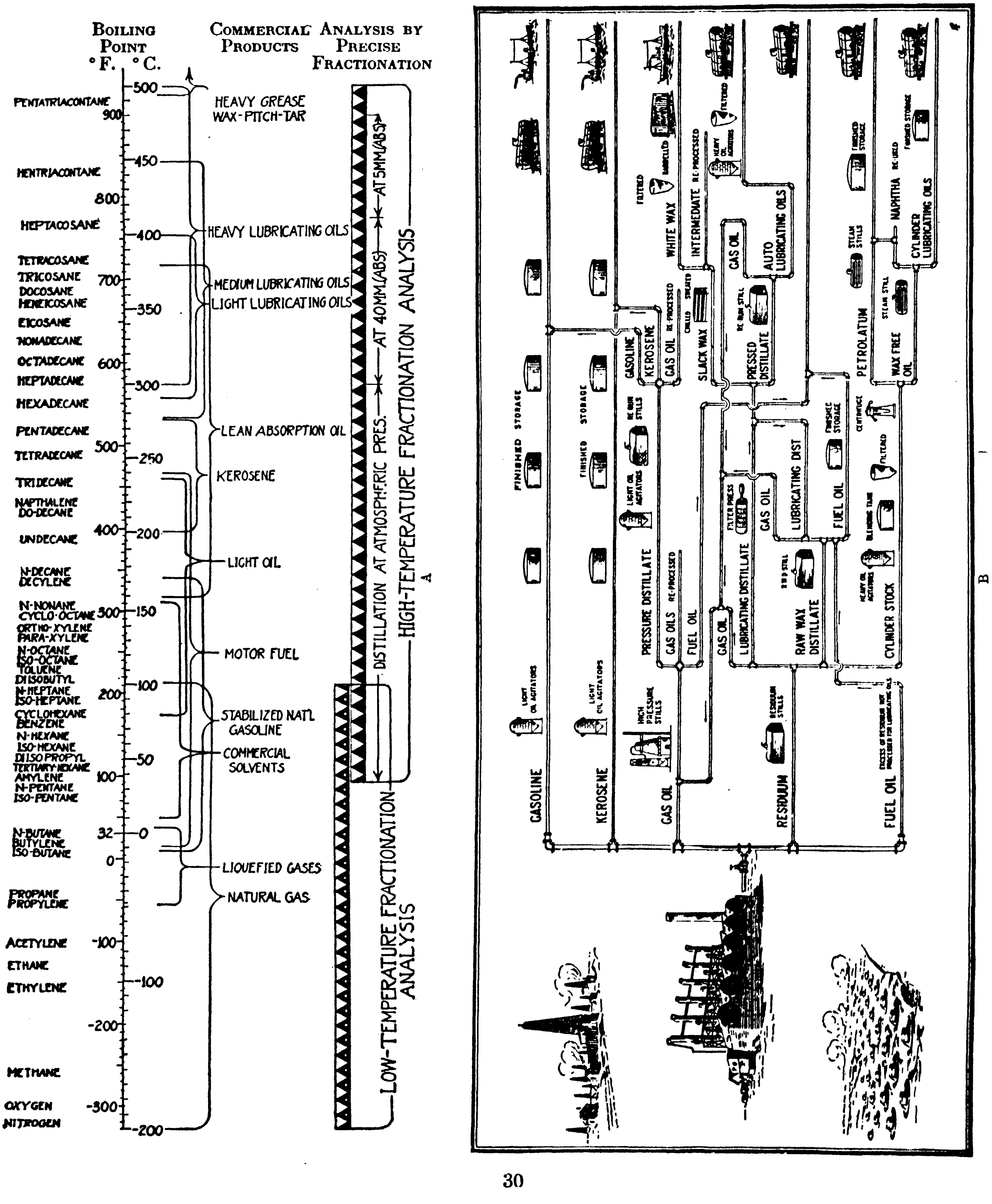

Fig. 15.—Schematic Outline of Petroleum Refining and Commercial Products Obtained.

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EXPT. 7. DISTILLATION OF PETROLEUM

1. In this experiment, why do you use a distilling flask with a low side-arm?

2. Why change from a water-cooled condenser to an air-cooled one at 150°?

3. What main class of hydrocarbons is present in petroleum?

4. List the hydrocarbons of the paraffin series that have boiling points (*a*) between the initial boiling point and 150° and (*b*) between 150°–300°.

5. Why are the crude gasoline and kerosene fractions washed with concentrated H_2SO_4?

6. Explain the result obtained in Expt. (*c*).

7. What products would you expect if you were to heat the residue in the distilling flask above 300°?

8. What would be the product if the residue were distilled to dryness?

9. When should you use (*a*) the high side-arm, (*b*) the medium side-arm, and (*c*) the low side-arm distilling flasks shown in Fig. 10?

10. Name ten important commercial products derived from petroleum.

11. What is meant by the following terms in reference to petroleum products:
    (*a*) Flash point.

    (*b*) Fire test.

    (*c*) 68°–72° naphtha.

    (*d*) "Cracking" of hydrocarbons.

12. Explain the purpose of the adapter.

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PREPARATION OF AN OLEFIN HYDROCARBON

EXPT. 8. ETHYLENE

Preparation.

Put 50 cc. of syrupy orthophosphoric acid into the 200 cc. flask. Set up the apparatus as shown in Fig. 16. Use rubber stoppers. The acid is heated to 220° and kept at this temperature while ethyl alcohol (C_2H_5OH) is added slowly, drop by drop, from the funnel. A steady stream of ethylene is produced. *Keep the flame continuously under the flask.* Collect three bottles of the gas by displacement of water, as in the methane experiment. Fill the fourth bottle with water to one-twelfth of its capacity and displace this volume of water with ethylene. Cover the bottles of gas with glass plates and keep in an inverted position until used.

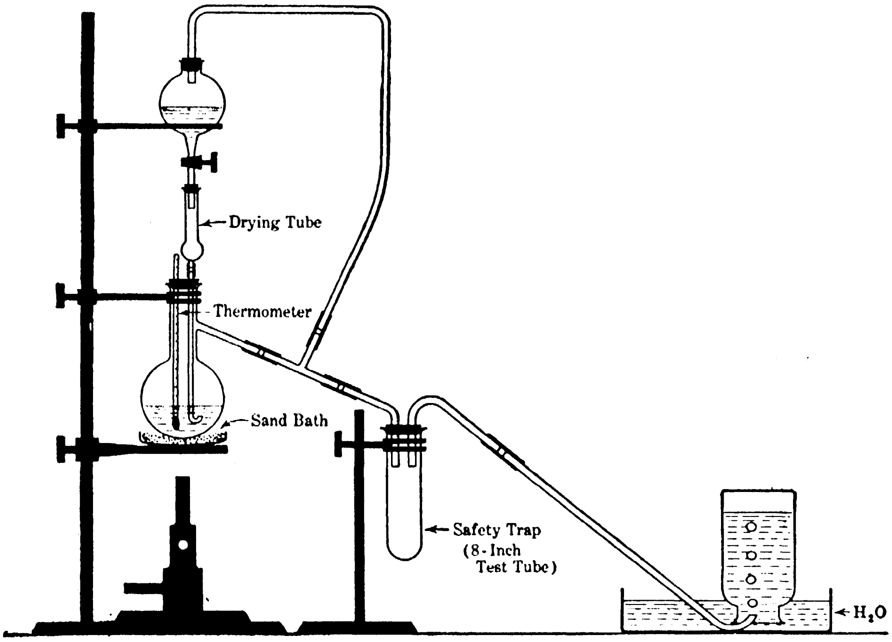

FIG. 16.

Properties.

(*a*) **Explosive Mixture of Ethylene and Air.**—Introduce a lighted match into the bottle containing the ethylene and air mixture. **Result:**—

(*b*) **Flammability and Products of Combustion.**—Ignite a bottle of ethylene. Hold a dry bottle over the burning gas and observe the moisture formed. Test for CO_2. **Result:**—

(*c*) **Ethylene and $KMnO_4$.**—Add 5 cc. of a $KMnO_4$ solution (0.01 per cent) to a bottle of ethylene. Replace the cover glass and shake well. **Result:**—

(*d*) **Ethylene and Bromine.**—Introduce *1 drop* of bromine into a bottle of the gas. (*Do not allow bromine to come in contact with your skin. Do not breathe bromine vapor.*) Replace the cover glass and shake well. (Do not invert the bottle.) Observe the oily droplets.

Blow over the mouth of the bottle. **Result:—**

Also test the gas in the bottle by holding a piece of moist blue litmus paper at the mouth. **Result:—**

Add 2 cc. of 10% NaOH solution, shake and **note the odor:—**

(*e*) **Test for Unsaturated Hydrocarbons in Illuminating Gas.**—Collect a bottle of illuminating gas (not natural gas) over water. Add 5 cc. of the dilute $KMnO_4$ solution as in Expt. (*c*) and shake. **Result:—**

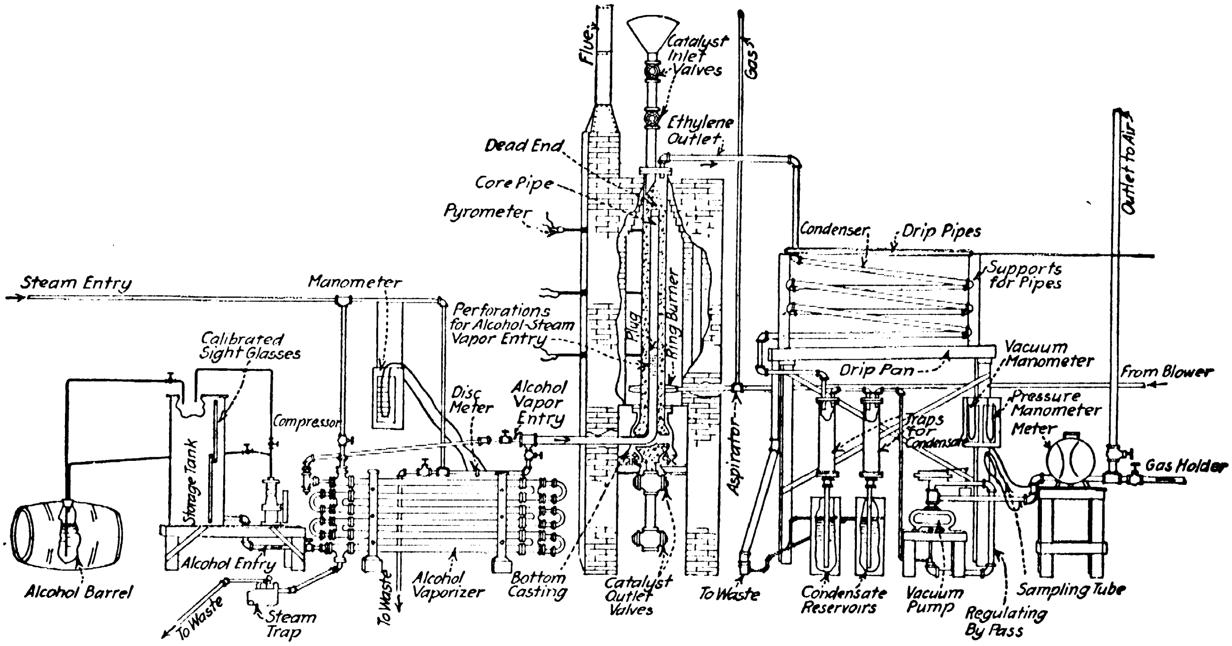

Fig. 17.—Experimental Installation for the Production of Ethylene by Kaolin Procedure.

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EXPT 8. ETHYLENE

1. Write the equations for the reactions involved in the preparation of ethylene.

2. What term is applied to this type of reaction?

3. Why is the phosphoric acid heated to 200° before the alcohol is added?

4. What other reagents may be used to produce ethylene from ethyl alcohol?

5. What is the advantage in using phosphoric acid in this preparation?

6. What other substances pass over with the ethylene? How can they be removed?

7. Write the equation for the reaction taking place in Expt. (*a*).

8. How does the luminosity of the ethylene flame compare with that of the methane flame? Is soot produced? Why?

9. Write the equation for the reaction taking place in Expt. (*c*).

Compare this reaction with the result obtained when methane was treated with $KMnO_4$ solution.

What is the significance of this test?

10. Write the equation for the reaction between ethylene and bromine. Give two names to the product formed.

Was HBr produced in Expt. (*d*)? Compare this result with that obtained in the analogous experiment with methane.

What term is applied to this type of reaction?

11. What conclusions can be drawn as to the presence of unsaturated hydrocarbons in illuminating gas? What is their value in illuminating gas?

12. List the physical properties of ethylene which you have observed.

13. Why is the tube in the distilling flask curved upward?

14. Why is the bulb of the thermometer placed in the liquid in this experiment while in distillations it is placed opposite the side-arm?

15. From your study of Fig. 17 outline the *essential* steps in the production of ethylene from alcohol.

16. What are some of the uses of ethylene?

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EXPT. 9. ACETYLENE

Preparation.

Arrange the apparatus as shown in Fig. 18. Place 10 g. of calcium carbide in the dry 250 cc. bottle. Allow water to drop slowly from the dropping funnel and collect the evolved gas by displacement of water

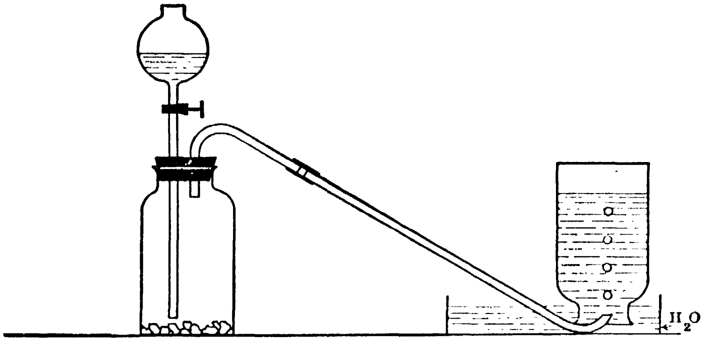

FIG. 18.

e methane experiment. Collect 5 bottles of the gas. Also prepare an explosive mixture of acetylene in the same manner as in the ethylene experiment (1 part of acetylene to 15 parts of air). As soon as you have collected the gas put your generator under the hood. Discard the first bottle.

Warning.—*Keep flames away. Do not allow the gas to escape into the room since it forms explosive mixtures with air and has an unpleasant odor.*

Properties.

(*a*) **Flammability.**—(Hood.) Ignite a bottle of the gas. **Result:**—

While the gas is burning, blow hard across the mouth of the bottle. **Result:**—

(*b*) **Explosive Mixture.**—Introduce a lighted match into the bottle containing the mixture of acetylene and air. **Result:**—

(*c*) **Acetylene and Bromine.**—Introduce 1 drop of bromine (*Caution*) into a bottle of the gas. Replace the cover glass immediately and shake. (Do not invert the bottle.) **Result:**—

Test the gases in the bottle with a piece of moistened blue litmus paper, holding it in the mouth of the bottle. **Result:**—

Add 2 cc. of 10% NaOH solution, shake and note the odor. **Result:**—

(*d*) **Acetylene and $KMnO_4$.**—Add to a bottle of the gas 3 cc. of $KMnO_4$ solution (0.01 per cent). Replace the cover immediately and shake. **Result:**—

(*e*) **Formation of Copper Acetylide.**—Add 5 cc. of an ammoniacal solution of cuprous chloride * to a bottle of the gas. Replace the cover and shake. **Result:**—

---

* Dissolve 1 g. of copper oxide in 15 cc. of conc. HCl and 5 cc. of water. As soon as the oxide has dissolved add 2 g. of copper filings or copper foil and boil until the solution becomes clear. Cool, decant 5 cc. of the liquid and make the solution ammoniacal.

Filter off the precipitate, wash with water, and dry on a water bath. Place about 0.1 g. on a crucibl cover and ignite. **Result:—**

Add dilute HCl (1 : 10) to the remainder of the precipitate and note the odor. **Result:—**

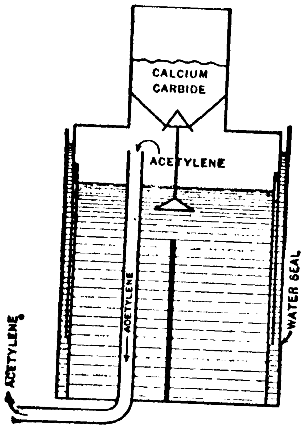

Fig. 19.—Acetylene Generator.

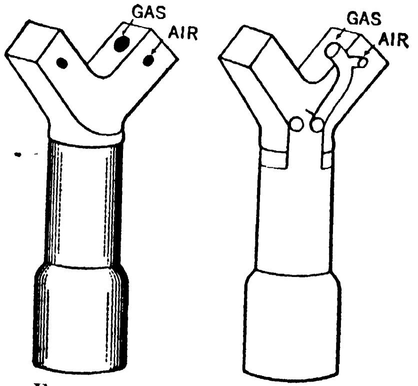

Fig. 20.—Acetylene Burner.

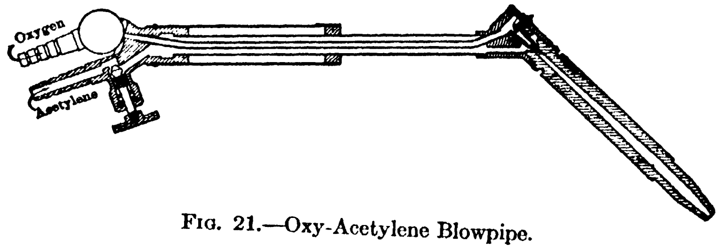

Fig. 21.—Oxy-Acetylene Blowpipe.

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EXPT. 9. ACETYLENE

1. Write the equation for the reaction involved in the preparation of acetylene.

2. Why is the first bottle of the collected gas discarded?

3. How does the acetylene flame compare in luminosity with those of methane and ethylene? Is soot produced? Why do you get a different effect when you blow across the mouth of the bottle of burning gas?

4. Write the equations for the reactions in Expt. (*c*).

5. Describe the physical appearance and odor of the products obtained in Expt. (*c*).

6. Give the formula and two names for each of the products which may be present in Expt. (*c*).

7. How might acetylene be obtained from the di- and tetra-halogen products obtained in Expt (*c*)? Write equations.

8. What does the test with blue litmus paper indicate?

9. What does the $KMnO_4$ test show about acetylene in Expt. (*d*)?

10. Which is the more unsaturated compound—ethylene or acetylene? Upon what experimental fact do you base your answer?

11. Write the equations for the reactions taking place in Expt. (*e*) and name the compounds produced.

12. For what type of group or linkage is Expt. (*e*) considered a test?

13. Would (*a*) methyl acetylene or (*b*) dimethylacetylene react with ammoniacal CuCl? Give reason.

14. What other metallic compounds form acetylides with acetylene?

15. What can you say about the stability of some of these metallic compounds?

16. Give another name for calcium carbide.

17. Make a list of the physical properties of acetylene observed in your experiment.

18. By means of the experimental facts observed in the experiments on methane, ethylene and acetylene, outline a chemical method to distinguish between these hydrocarbons.

19. What is the function of the air inlet in Fig. 20?

20. What are the uses of acetylene?

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PREPARATION OF AN ALKYL HALIDE

EXPT. 10. ETHYL IODIDE

Preparation.

Introduce 3 g. of red phosphorus and 25 cc. of absolute alcohol (for preparation see Expt. (*g*) p. 55), into the distilling flask. Add 30 g. of finely powdered iodine in small portions (about 3 g. at a time), shaking after each addition. Replace the reflux condenser (Fig. 22) after each portion is added. If the reaction becomes too violent (boils), cool the flask by immersing in cold water until the reaction has subsided. When all the iodine has been added and the reaction has subsided, let the water drain from the condenser. Attach a drying tube filled with anhydrous $CaCl_2$ to the condenser and allow the reaction mixture to stand until the next laboratory period. Heat the mixture on a water bath, with the reflux condenser still attached to the flask, for 1½ hours. Cool. Then remove the reflux condenser and arrange the apparatus as shown in Fig. 23. Distill from the water bath until no more liquid passes over. If bumping occurs this can be eliminated by using a few glass beads. Transfer the distillate to a small separatory funnel. Add 20 cc. of water and shake thoroughly. Allow the liquids to separate. Draw off the lower layer (ethyl iodide) into a small beaker and discard the aqueous layer. Now pour the contents of the beaker into the separatory funnel, add 10 cc. of 5 per cent NaOH solution and shake. Allow the liquids to separate and draw off the lower layer into a small dry flask. Add about 1 g. of anhydrous calcium chloride, stopper securely and allow to stand until the next laboratory period. Then filter through glass wool or asbestos into a dry 50 cc. distilling flask, being careful not to decant any of the calcium chloride solution which may be present. Distill through a water condenser into a dry receiver. Collect the fraction boiling between 71°–73°. Ethyl iodide boils at 72.3°.

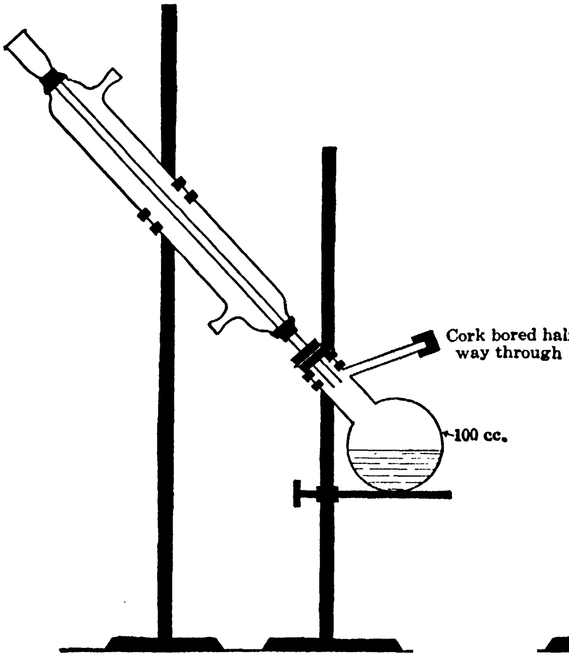

Fig. 22.

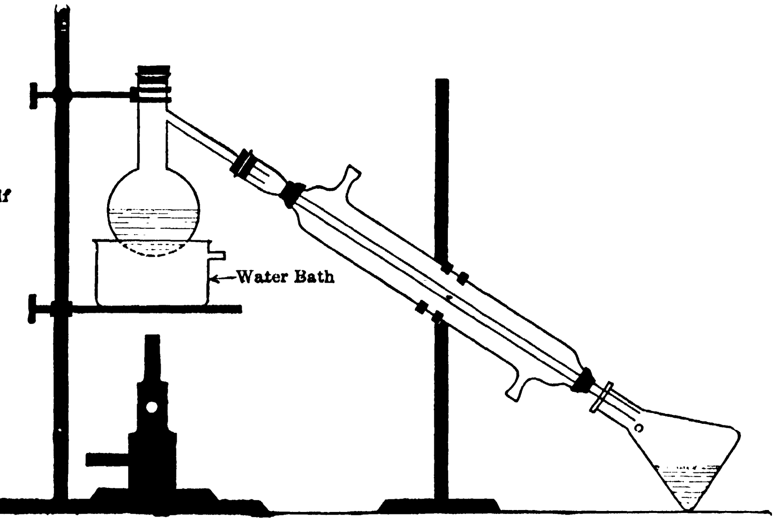

Fig. 23.

Yield = g.

Calculations:—

$$P + 3I \rightarrow PI_3$$

$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$$

$$3I : 3C_2H_5I :: 30 : x$$

$x =$ g. of ethyl iodide

This gives the theoretical yield. What is your percentage yield in this experiment?

Properties.

(*a*) **Action of Silver Nitrate on Alkyl Halides.**—To a suspension of a few drops of ethyl iodide in water add 1 cc. of a silver nitrate solution (10 per cent) and shake. **Result:—**

Repeat using (*a*) ethyl bromide and (*b*) ethylene chloride instead of ethyl iodide. Allow to stand until the next laboratory period. **Results:—**

Also try the action of silver nitrate solution on pure chloroform. **Result:—**

(*b*) **Action of Aqueous NaOH on Ethyl Iodide.**—To 5 drops of ethyl iodide in a 20 cm. test tube add 15 cc. of a sodium hydroxide solution (30 per cent). Attach a reflux condenser and heat on a water bath for an hour. Cool, make slightly acid with dilute nitric acid and test a portion for ethyl alcohol, using the iodoform test. Expt. (*k*), (p. 56). **Results:—**

(*c*) **Action of Alcoholic NaOH on Ethylene Bromide.**—In a 20 cm. test tube dissolve 1 g. of NaOH in 10 cc. of alcohol. Add 2 cc. of ethylene bromide. Attach a delivery tube and support the test tube at an angle of about 45°. Heat gently and collect successively 1 small and 1 large test tube of the gas by displacement of water without interruption. To the large test tube add 3 cc. of a freshly prepared clear solution of ammoniacal CuCl (p. 37). Filter, wash, and examine filter paper. **Result:—**

(*d*) **Action of Light on Ethyl Iodide.**—Take two test tubes. In each place about 2 cc. of the colorless ethyl iodide. Expose one tube to strong sunlight; put the other in a dark place. After two hours examine the tubes. **Results:—**

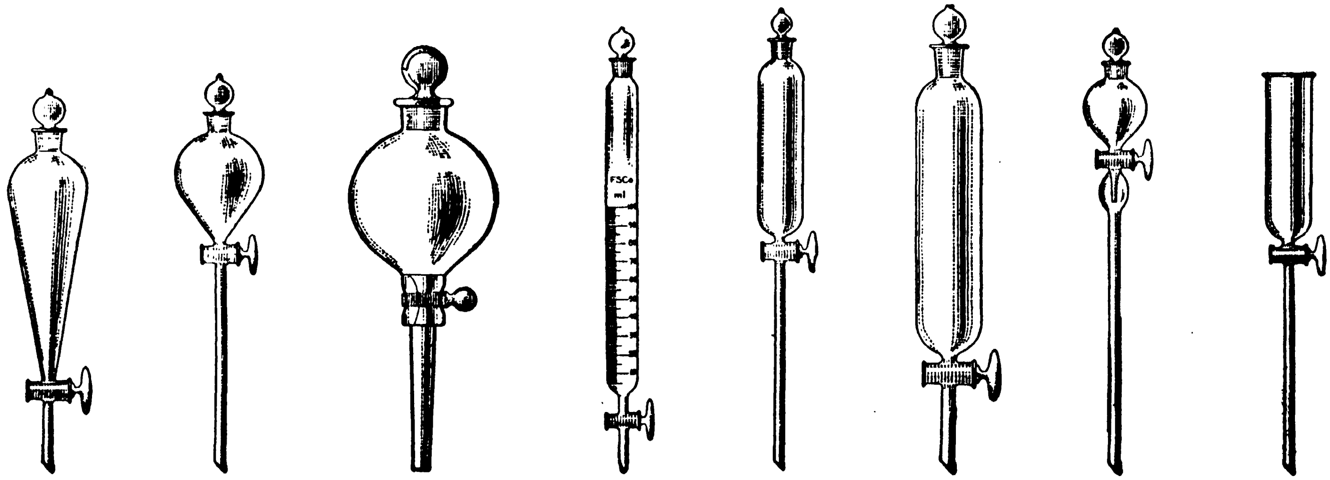

Fig. 24.—Separatory and Dropping Funnels.

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EXPT. 10. ETHYL IODIDE

1. Write the equations for the preparation of ethyl iodide.

2. Write the equation for the general type reaction for the preparation of alkyl halides by this method.

3. Why is absolute alcohol used in this preparation?

4. What is the purpose of the reflux condenser?

5. Why is the reaction mixture refluxed on a water bath and not directly over a wire gauze?

6. Explain how glass beads and other agents eliminate " bumping."

7. Why is the crude ethyl iodide washed first with water and subsequently with NaOH solution?

8. Why is the ethyl iodide filtered through glass wool or asbestos instead of filter paper?

9. Explain the difference between a dehydrating agent and a drying agent.

10. What are your conclusions from Expt. (*a*) as to the relative reactivities of halogens in organic compounds with $AgNO_3$ solution?

11. Write the equations for the reactions in Expt. (*b*).

12. Write the equation to show the action of alcoholic NaOH on ethylene bromide as in Expt. (*c*).

13. What substance is responsible for the change of color in the tube exposed to sunlight in Expt. (*d*)?

14. How do you explain the influence of light on organic compounds?

15. What special advantage has the 7th funnel in Fig. 24 over the 2nd?

16. How do (*a*) boiling points and (*b*) specific gravities of normal RCl, RBr and RI compounds vary with increasing molecular weight?

17. Give an important use for ethyl chloride.

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EXPT. 11. CHLOROFORM

Preparation.

Warning:—Do not add acetone to dry H T H.

Introduce 350 cc. of water into a round-bottom liter flask and add 110 g. H T H. "high test hypochlorite" (contains approximately 65% available chlorine). Place the flask in a pan of cold water and attach a reflux condenser. Through the top of the condenser **add at five-minute intervals 5 cc. portions of acetone until a total of 25 cc. has been introduced. Shake and cool the contents of the flask after each addition.**

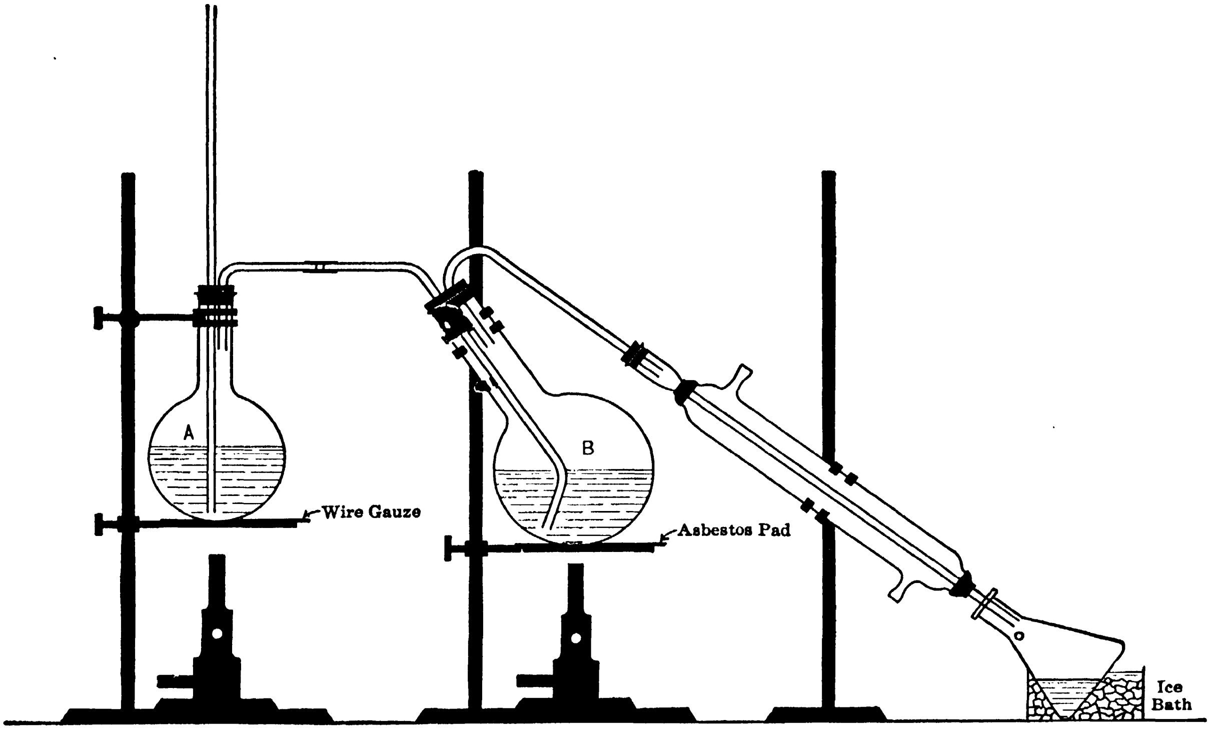

FIG. 25.

When all the acetone has been added, reflux the mixture on a water bath for fifteen minutes. Cool to room temperature. Set up the apparatus as shown in Fig. 25. Introduce about a quarter gram of paraffin into the reaction flask (B) to reduce frothing. Before lowering the steam inlet tube to the bottom of the flask (B), have steam generated in flask (A). Pass steam from flask (A) through the reaction flask (B) until no more chloroform distills. This may be ascertained by collecting two or three cc. of distillate and noting whether any oily droplets of chloroform are present. If the distillate is clear and no oily droplets are present, discontinue the distillation. If any lime-water is carried over mechanically with the distillate, neutralize it with hydrochloric acid (10%). Transfer the distillate to a separatory funnel, draw off the lower (chloroform) layer and discard the upper (aqueous) layer. Wash the chloroform layer twice by shaking it vigorously in a separatory funnel with 10 cc. portions of water. Transfer the washed chloroform to a small Erlenmeyer flask and add about 2 g. of anhydrous calcium chloride. Stopper well and allow to stand until the next laboratory period. Then decant the chloroform into a dry 50 cc. distilling flask and distill from a water bath into a dry, weighed flask. Weigh the receiver with the chloroform and calculate the per cent yield of chloroform from the weight of acetone used.

Yield = g. Calculated = g. Percentage yield =

PRINCIPLE OF STEAM DISTILLATION

Steam distillation is a method often used in organic chemistry for the separation or purification of compounds. Every substance has a definite vapor pressure at a given temperature. If a substance is vaporized with steam, the resulting vapor will be a mixture of two kinds of molecules (water and the substance). Each species of molecule will exert its own vapor pressure proportional to the number of molecules present. Let us take a mixture of two liquids which are immiscible, for example nitrobenzene and water. If this mixture is heated, the vapor pressure of each component increases. But each component exerts its own vapor pressure independently of the other. When the sum of the vapor pressures of the two compounds equals the atmospheric pressure, the mixture begins to boil. Distillation continues without change in composition of the distillate until one of the components is entirely distilled over. In this particular case the boiling point of the mixture is 99° at 760 mm. Under these conditions water has a vapor pressure of 733 mm. Therefore, the vapor pressure of the nitrobenzene must be the difference between 760 mm. and this figure, i.e., 27 mm. Avogadro's hypothesis states that under the same conditions of temperature and pressure equal volumes of gases contain the same number of molecules. Under the conditions of this experiment, where the temperature is the same but the pressure is different, the number of molecules in the same volume will be proportional to the pressure. Hence, in the above example, for every 733 molecules of water there must be 27 molecules of nitrobenzene present. The molecular weight of water is 18, that of nitrobenzene is 123. Therefore the weights of water and of nitrobenzene distilling over will be in the proportion of 733 × 18 to 123 × 27, or approximately 4 : 1.

From the above discussion it is seen that although the vapor pressure of the nitrobenzene is only $\frac{1}{27}$ that of water, $\frac{1}{5}$ of the distillate (by weight) consists of nitrobenzene. This is due to the high molecular weight of nitrobenzene as compared with water, i.e., the high molecular weight makes up in yield for the low vapor pressure. It is this fact which makes steam distillation practicable.

Properties.

(*a*) **Odor.**—Note the odor of chloroform.

(*b*) **Flammability.**—Put 5 cc. of chloroform in an evaporating dish. Heat gently and hold a lighted match in the vapor. **Result:**—

(*c*) **Test for Chloride.**—Shake 10 drops of chloroform with 5 cc. of distilled water. Test with $AgNO_3$ solution. **Result:**—

If AgCl forms it is due to impurities present.
Repeat Beilstein's test for halogens. (Expt. *e*1, p. 12.) **Result:**—

(*d*) **Oxidation of Chloroform.**—To 10 drops of chloroform add a crystal of potassium dichromate and 1 cc. of conc. H_2SO_4 and heat gently. Carefully note the odor of the gas evolved. **Result:**—

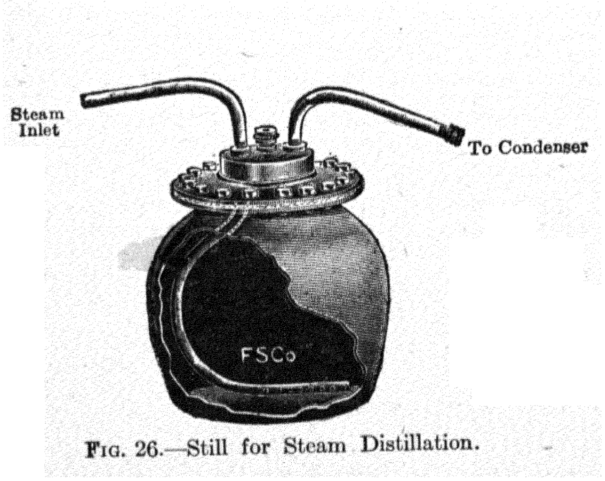

Fig. 26.—Still for Steam Distillation.

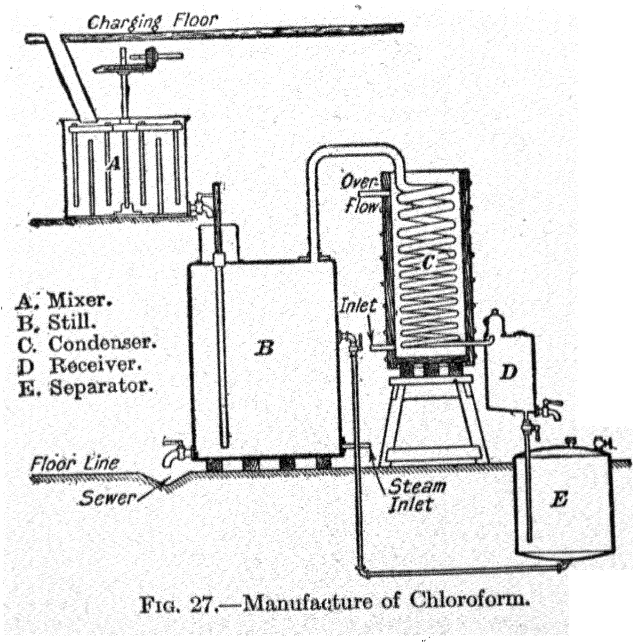

Fig. 27.—Manufacture of Chloroform.

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EXPT. 11. CHLOROFORM

1. Explain the principle of steam distillation.

2. Write the equations for the preparation of chloroform as performed in this experiment.

3. What observation shows the fact that all the chloroform has been distilled over with steam?

4. Why is crude chloroform washed with water?

5. Why do you not obtain a precipitate in Expt. (*c*)?

6. Write equations for the reactions in Expt. (*d*). Name the organic compound formed.

7. In conducting the steam distillation for the preparation of chloroform, what other compounds pass over into the distillate?

8. From the results of Expt. (*b*) can you suggest a use for chloroform? Why is it not used for this purpose? What halogen compound is used?

9. Why is chloroform kept in amber-colored bottles?

10. Chloroform used for anesthesia contains 1 per cent alcohol. Why?

11. In general, when should the receiver (Fig. 25) be kept in an ice bath during distillation?

12. In Fig. 27,
    (*a*) What chemicals are placed in *A*?

    (*b*) What products distill from *B*?

    (*c*) What is the waste product discharged from *B*?

    (*d*) What separates in *E*?

13. Compare the individual parts of equipment of Fig. 27 with those of Fig. 25.

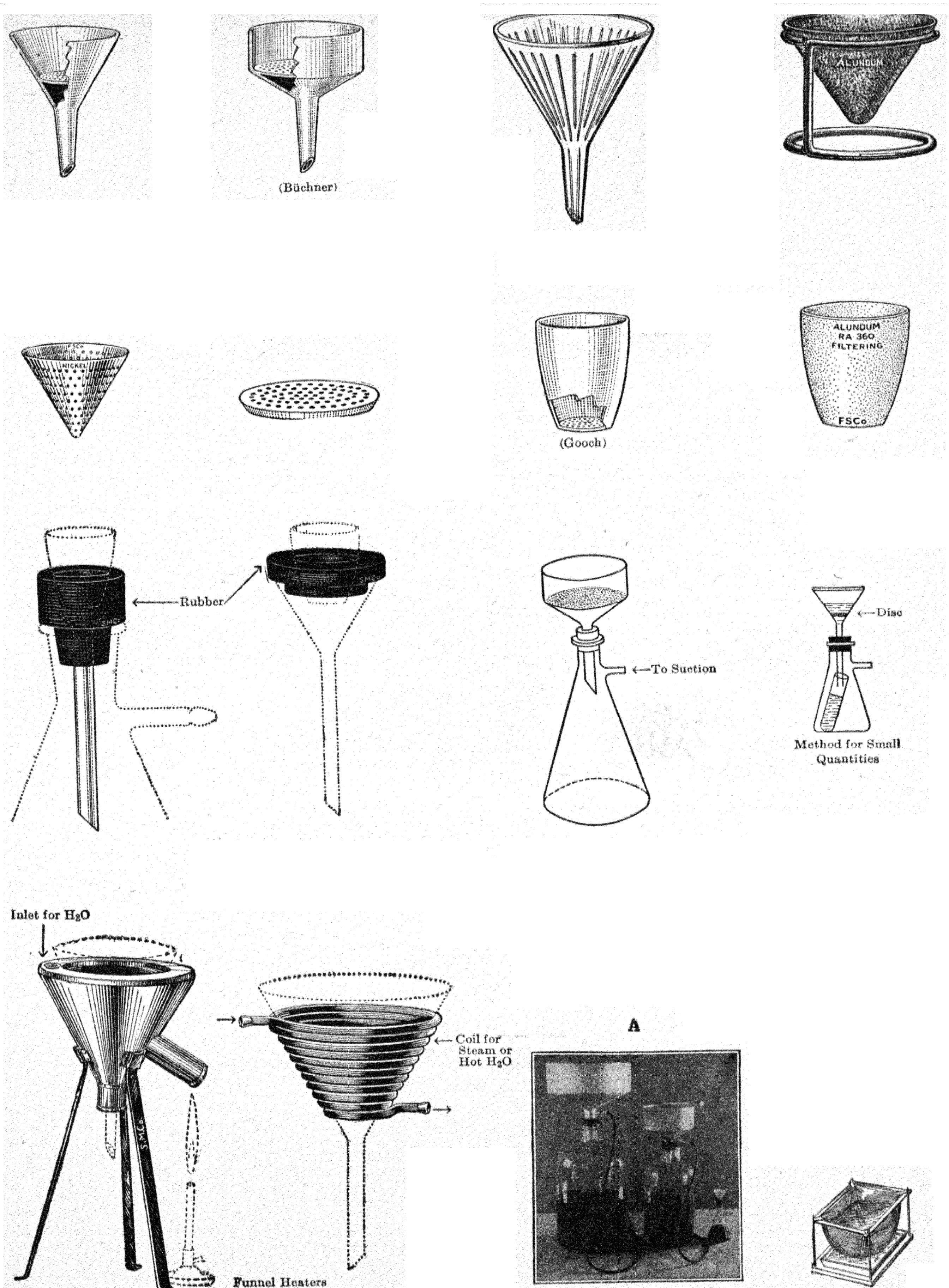
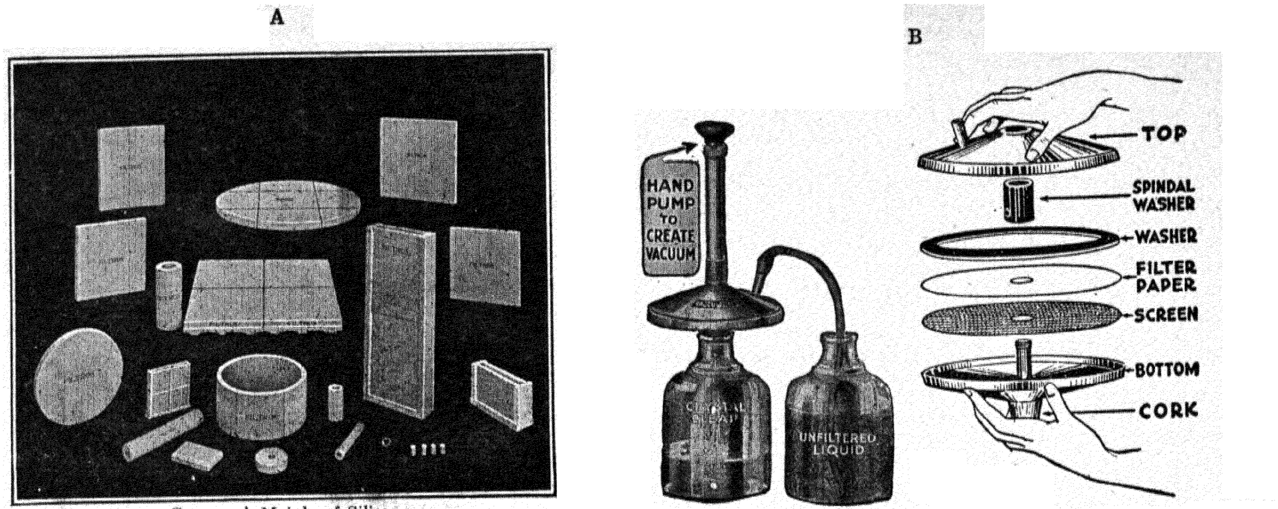
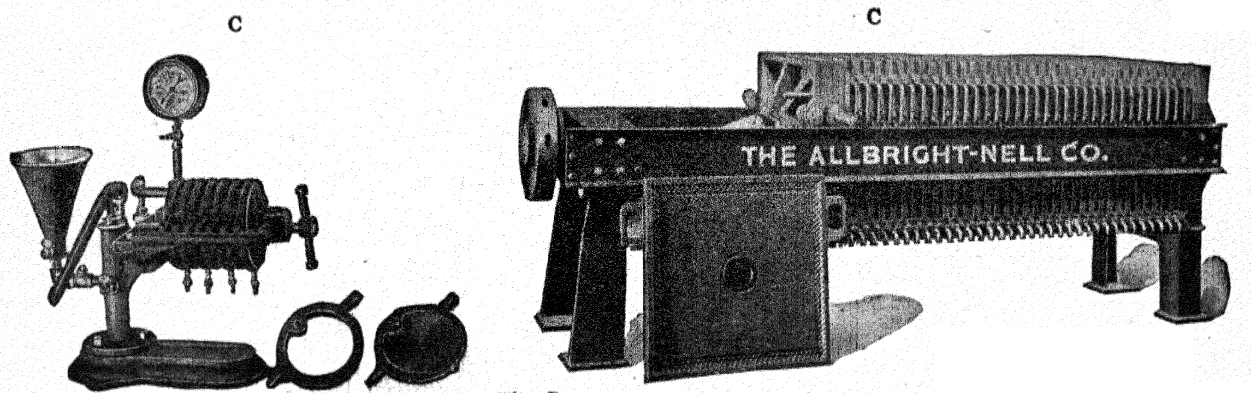


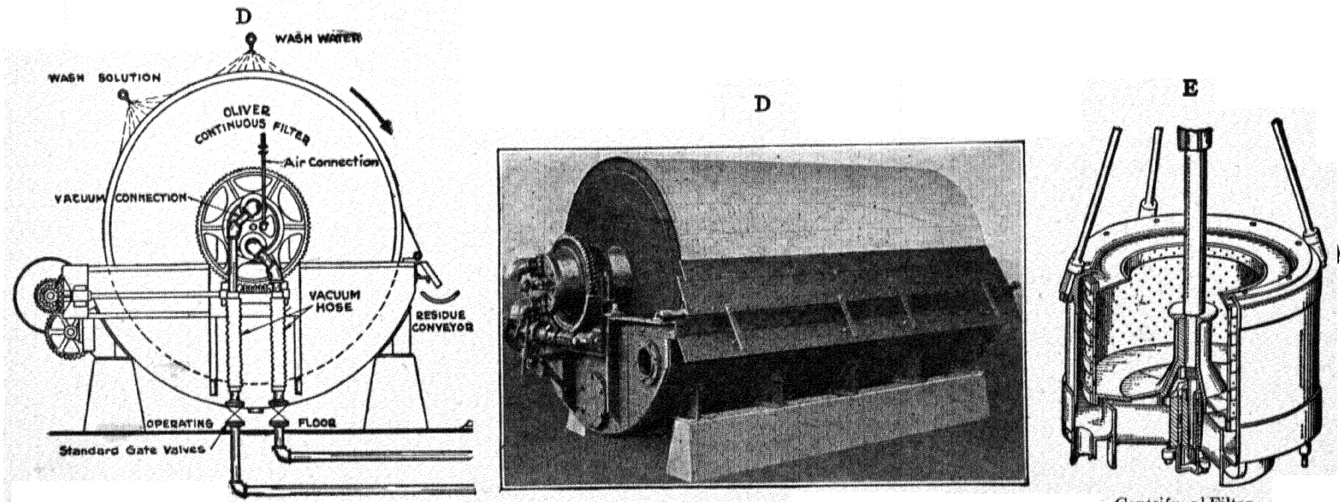
Fig. 28.—Laboratory Filtering Devices.



Composed Mainly of Silica.



Filter Presses



Filter Press

Centrifugal Filter

Fig. 29.—Filtering Devices.

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EXPT. 12. METHANOL

Properties.

NOTE.—Methanol (commonly known as wood alcohol) is poisonous.

(*a*) **Odor.**—Note the odor of methanol.

(*b*) **Solubility.**—Shake 5 cc. of methanol with 5 cc. of water. **Result:**—

(*c*) **Flammability.**—Pour 3 cc. of methanol into a small evaporating dish and ignite. Hold a clean dry bottle above the flame and collect the products of combustion. Note the moisture collecting in the bottle. Invert the bottle, add 10 cc. of lime-water, cover it and shake. **Result:**—

(*d*) **Sodium and Methanol.**—To 5 cc. of pure methanol add **a small** piece of sodium (size of a pea). Test the gas generated by bringing the mouth of the tube to a flame. **Result:**—

Extinguish the flame by covering the mouth of the test tube with an asbestos pad. After the evolution of gas has ceased, evaporate the solution to dryness on a water bath. **Result:**—

Dissolve the residue in water and test the solution with red litmus paper. **Result:**—

(*e*) **Methanol and Anhydrous $CaCl_2$.**—Heat 2 cc. of methanol with 1 g. of *pulverized* anhydrous $CaCl_2$ at 50° for a period of 10 minutes in a water bath. Shake occasionally. Cool, stopper and set aside until the next laboratory period. **Result:**—

Heat the test tube to expel the methanol and burn it at the mouth of the tube. What remains in the tube?

(*f*) **Oxidation of Methanol.**—Heat a coil of copper wire (prepared by winding the wire around a pencil 6 times) to redness in the upper oxidizing part of a flame. Plunge this, while still at red heat, into a test tube containing 5 drops of methanol. Repeat this operation twice. Note the color of the copper wire before inserting it in the methanol and after its removal. Smell the contents of the test tube. **Result:**—

Test for the formaldehyde produced. Add 3 cc. of water and 2 drops of a 1 per cent solution of resorcinol. Shake well and then carefully pour this solution down the side of a test tube held in an inclined position containing 5 cc. of conc. H_2SO_4. Do not shake. Note the color of the ring at the junction of the two liquids. **Result:**—

(*g*) **Methanol as a Solvent.**—Test the solubilities of ½ g. of each of the following substances in 5 cc. of methanol: shellac, rosin, fat, sugar and camphor. **Results:**—

(*h*) **Test with Litmus Papers.**—Test methanol with moist litmus papers. **Results:**—

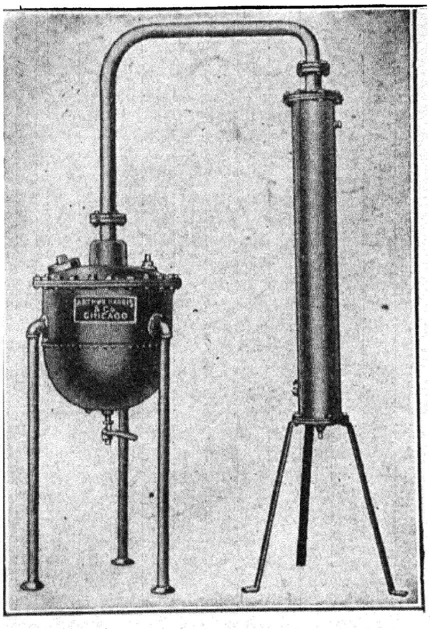

Fig. 30.—Industrial Distillation Apparatus.18.

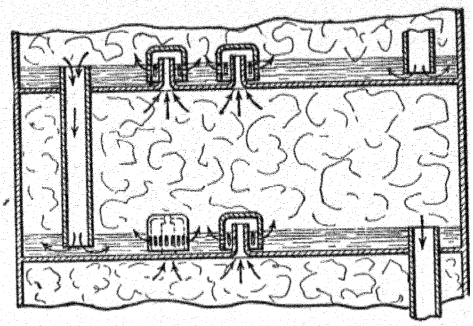

Fig. 31.—Section of a Fractionating Column.

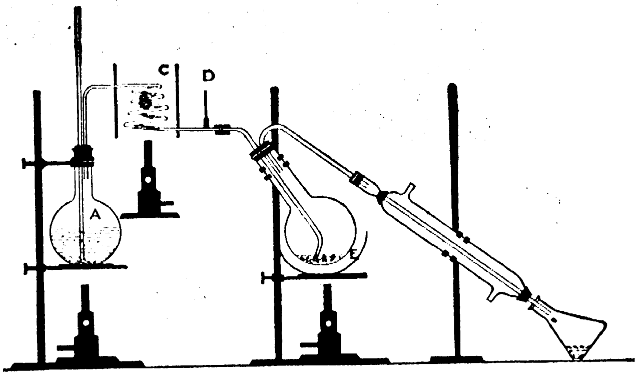

Fig. 31A.—Distillation with Superheated Steam.

A—Steam Generator
B—Superheater
C—Air Bath
D—Thermometer
E—Oil Bath

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Section. . . . . *Date*. . . . .

EXPT. 12. METHANOL

1. Write the equation for the combustion of methanol.

2. Write the equation for the action of sodium on methanol and give two names to the organic compound formed.

3. Write the equation to show the alkalinity of the residue in Expt. (*d*).

4. Mention other inorganic compounds that form complexes with methanol besides the one given in Expt. (*e*).

5. Define and illustrate (*a*) water of crystallization and (*b*) alcohol of crystallization

6. Write the equation for the oxidation of methanol in Expt. (*f*).

7. Why is it necessary to heat the copper wire first in Expt. (*f*)?

8. What compound would be formed if the formaldehyde in Expt. (*f*) were further oxidized?

9. Mention a number of industries in which methanol is employed as a solvent.

10. The formula for methanol is CH_3OH. Why is there no effect on litmus paper in Expt. (*h*)?

11. Mention the well-known specific physiological effect of methanol.

12. What are the present sources of methanol?

13. When are the funnel heaters shown in Fig. 28 used?

14. Draw a diagram of Fig. 30 and label parts.

How is this still heated?

15. What is the advantage of distillation by superheated steam (Fig. 31A) over steam distillation.

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EXPT. 13. ETHYL ALCOHOL

Preparation.

Dissolve 20 g. of glucose in 200 cc. of water. Make a paste (by grinding) of one-fourth of a cake of yeast with 20 cc. of water. Introduce the glucose solution and the yeast paste, together with 10 cc. of Pasteur salts* into bottle (*A*). Also add 5 g. of corn meal. Fill the bottle (*B*) about one-third full of clear lime-water and add 10 cc. of kerosene. Arrange the apparatus as shown in Fig. 32 and allow it to stand until the next laboratory period. Filter about half of bottle (*A*) through cotton into a distilling flask, add 2 g. of Na_2CO_3 and with a low flame distill over about 15 cc. Test for ethyl alcohol in the distillate as indicated in Expts. (*k*) and (*l*) in this experiment.

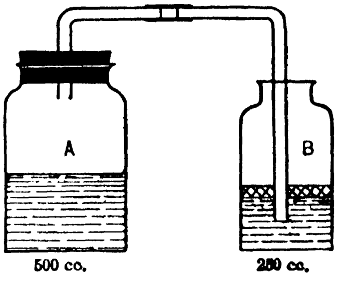

FIG. 32.

Properties.

(Use ethyl alcohol from the stock room).

(*a*) **Color.**—Note the color of alcohol.

(*b*) **Odor.**—Note the odor.

(*c*) **Ethyl Alcohol as a Solvent.**—Put 1 g. of iodine into a test tube. Add 15 cc. of ethyl alcohol and warm gently in a water bath. **Result:**—

To 1 cc. of lemon oil add 5 cc. of ethyl alcohol and shake. **Result:**—

Test the solubilities of ½ g. of each of the following substances in 5 cc. of ethyl alcohol: fat, sugar, rosin, camphor, etc. **Results:**—

(*d*) **Flammability of Alcohol.**—Place 2 cc. of alcohol in an evaporating dish and ignite. **Result:**—

(*e*) **Test with Litmus.**—Test the alcohol with litmus papers. **Results:**—

(*f*) **Presence of Water.**—To 10 cc. of alcohol add 1 g. of anhydrous copper sulfate, which may be prepared by heating the blue hydrated copper sulfate in a porcelain crucible or dish until it is converted into the white anhydrous form. **Result:**—

(*g*) **Preparation of Absolute Alcohol.**—Into a 300 cc. flask introduce 75 cc. of alcohol, and add small lumps (not powder) of quicklime until the lumps reach to the surface of the liquid. Stopper the flask with a cork carrying a drying tube filled with anhydrous $CaCl_2$ and allow it to stand until the next laboratory period. At the end of this time connect the flask with a reflux condenser having a drying tube filled with $CaCl_2$ attached at the upper end and reflux on a water bath for an hour. (Flask is to be placed *above* and not *in* the boiling water.) Then remove the reflux condenser and arrange for distillation from a water bath. A dry suction flask, see Fig. 34 (p. 59), is attached to the condenser by means of a cork. To the side-arm of the suction flask is attached a drying tube filled with anhydrous $CaCl_2$. Note the temperature at which the alcohol distills. Test the distillate according to Expt. (*f*) of this experiment. If it is not absolute, subject it to the same treatment again.

---

* Pasteur salts contain food necessary for the yeast plant. The solution contains:

Potassium phosphate..
Calcium phosphate..
Magnesium sulfate..
Ammonium tartrate..
Water:...

(*h*) **Heat Developed on Mixing Alcohol and Water and the Volume Change.**—Take two 20 cm. test tubes. Indicate by means of a blue pencil or a label the 10 cc. and 20 cc. marks on one and the 10 cc. mark on the other. These marks may be located by running in from a pipette first 10 cc. and then 20 cc. of water and making a mark on the outside of the tube directly opposite the upper surface of the water. Into the one having only the 10 cc. mark pour 10 cc. of absolute alcohol; into the other tube pour 10 cc. of distilled water. Bring these to the same temperature by allowing them to stand in a beaker of water for 20 minutes. Record the temperature. Then quickly pour the alcohol into the test tube containing the water and stir. Note any change in volume and in temperature.

(*i*) **Alcohol and Sodium.**—To 5 cc. of absolute alcohol add a small piece of sodium (about the size of a pea). Bring the test tube close to a flame and ignite the gas evolved. **Result:**—

(*j*) **Alcohol and Phosphorus Pentachloride.**—(Perform in hood.) To 5 cc. of absolute alcohol in a dry test tube add a pinch of PCl_5. **Result:**—

Refer to the experiment for the preparation of ethyl iodide (p. 41).

(*k*) **Iodoform Test.**—To 2 cc. of alcohol add 2 cc. of NaOH solution (10 per cent) and 5 cc. of water. Then add, drop by drop, a solution of iodine in potassium iodide until a permanent yellow precipitate is produced. Warm gently for a minute and set the tube aside. **Result:**—

Note the odor of the compound.

(*l*) **Ethyl Acetate Test.**—Place 2 cc. of alcohol, 2 cc. of glacial acetic acid, and 3 cc. of conc. H_2SO_4 in a test tube and heat gently. Waft the evolved product toward the nose and note the odor. **Result:**—

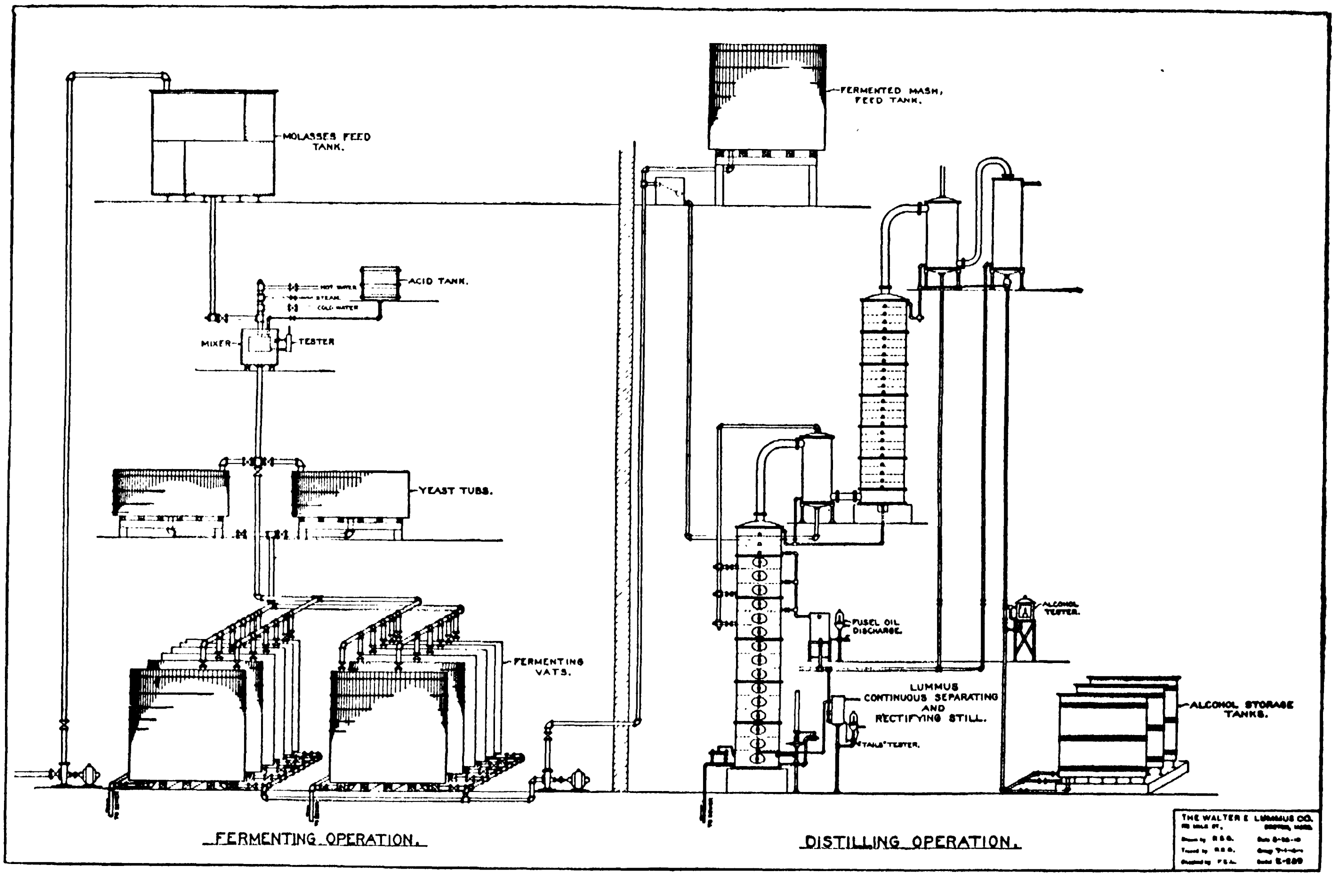

FIG. 33.—Alcohol Manufacture.

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EXPT. 13. ETHYL ALCOHOL

1. Explain the meaning of the terms (*a*) a ferment and (*b*) fermentation.

2. What is yeast and what is its source?

3. What is the purpose of Pasteur salts?

4. Write the equations for the preparation of alcohol by fermentation.

5. Why is the lime-water covered with a kerosene layer?

6. Why is Na_2CO_3 added before the alcohol is distilled?

7. Define and illustrate the terms (*a*) tincture and (*b*) essence.

8. How would you prove that a small amount of a substance is dissolved in alcohol?

9. Differentiate between absolute alcohol and 100 per cent alcohol.

10. Why do you use lumps of quicklime and not the powder?

11. How do you explain the decrease in volume in Expt. (*h*)? *

12. Write the equation for the reaction in Expt. (*i*).

13. Write the equation for the reaction in Expt. (*j*).

14. Write the equations, step by step, for the reactions in Expt. (*k*).

15. Write the equation for the reaction in Expt. (*l*).

16. Why is sulfuric acid added in Expt. (*l*)?

17. What are the meanings of the following terms:—(*a*) denatured alcohol, (*b*) medicated alcohol and (*c*) 190 proof alcohol?

*

18. What raw materials are used for the preparation of ethyl alcohol on an industrial scale?

19. Give the purpose of each labeled part of Fig. 33.

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EXPT. 14. ETHYL ETHER

Preparation.

Warning:—Keep all flames away from the receiver during the operation. NEVER BOIL ETHER OVER A FREE FLAME. Ether is very flammable.

Put 75 g. of ethyl alcohol into a 500 cc. distilling flask and add 75 g. of conc. H_2SO_4 (5 cc. at a time). Shake well after each addition and keep the mixture cool during the process of mixing. Then arrange the apparatus as shown in Fig. 34. When the temperature reaches about 140°, ether begins to distill over. Now add slowly through the dropping funnel 150 g. of alcohol so that the alcohol drops into the mixture at approximately the same rate as the ether distills over. During this addition the temperature should be held as close to 140° as possible. Continue heating for 5 minutes after all the alcohol has been added. Then transfer the distillate to a separatory funnel, add 25 cc. of NaOH solution (10 per cent) and shake. Draw off the lower layer. Add to the liquid (ether) remaining in the funnel one-half its volume of a saturated NaCl solution and shake. Wait until the layers separate. Discard the lower layer and run the liquid remaining in the funnel into a glass-stoppered bottle. Add about 2 g. of anhydrous $CaCl_2$, stopper and set aside until the next laboratory period. Then distill from a water bath, using the same type of receiver as above. Ether boils at 35°.

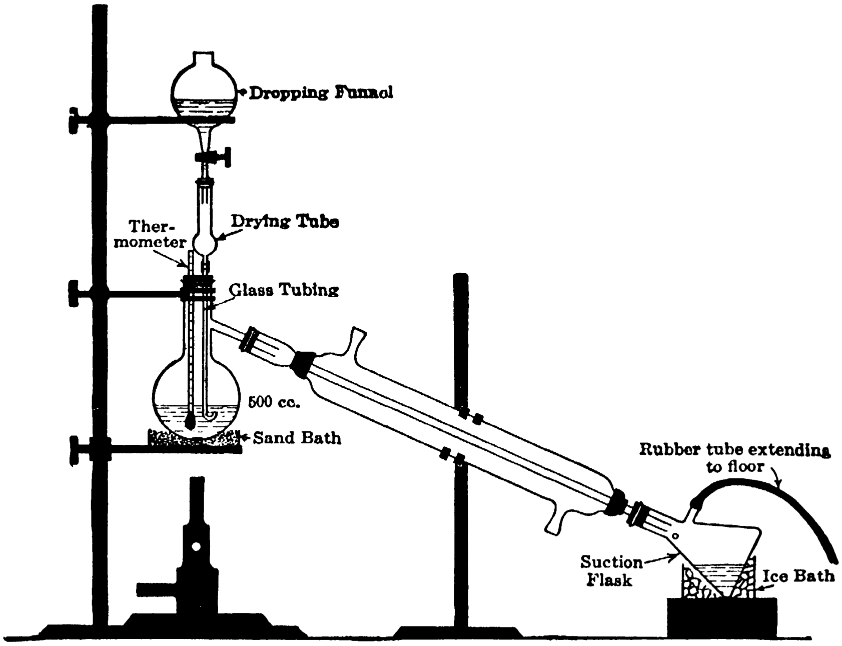

FIG. 34.

Yield = g. Calculated = g. Percentage Yield =

Properties.—(HAVE NO FLAMES NEAR WHEN WORKING WITH ETHER.)

(*a*) **Odor.**—Note the odor of ether.

(*b*) **Flammability of Ether.**—Dip a stirring rod into ether and hold it in the flame. Note the flammability and the color of the flame.

(*c*) **Ether and Litmus Paper.**—Shake a few drops of ether with 5 cc. of water and test with litmus papers. **Results:**—

(*d*) **Cooling Effect of Ether.**—Pour 2 cc. of ether in the palm of your hand. Blow across it. **Result:**—

(*e*) **Solvent Action of Ether.**—Into each of four test tubes pour 5 cc. of ether. Then put a crystal of iodine in the first, a small piece of paraffin in the second, a small piece of beeswax in the third, and a small portion of lard in the fourth. Shake the tubes thoroughly in each case. Pour off the liquids into separate watch glasses and allow to evaporate. **Results:**—

(*f*) **Solubility of Ether in Water.**—Agitate 1 cc. of ether with 15 cc. of water. **Result:**—

(*g*) **Solubility of Water in Ether.**—Shake 10 cc. of ether with 10 cc. of water in a test tube. Carefully decant a portion of the ether layer and add 0.5 g. of anhydrous copper sulfate. **Result:**—

(*h*) **Absolute Ether.**—Shake 100 cc. of commercial ether with 50 cc. of water in a separatory funnel. Separate the ether layer and transfer to a glass-stoppered bottle. Add 2 g. of anhydrous $CaCl_2$, stopper and allow to stand until the next laboratory period. Then decant the ether from the $CaCl_2$ into a 200 cc. distilling flask, stopper the side-arm and add about 2 g. of sodium in the form of very thin, freshly cut shavings. Insert a cork having a drying tube filled with $CaCl_2$. Shake frequently and when gas is no longer evolved, distill the ether from the sodium, using a water bath. The receiver (a dry suction flask with a calcium chloride tube attached to the side-arm) is firmly connected to the condenser by means of a cork. Test the distillate with anhydrous copper sulfate. **Result:**—

The sodium residue in the distilling flask should be transferred to the bottle on the reagent shelf, marked " Sodium Residues."

(*i*) **Ether and Sodium.**—To 5 cc. of absolute ether add a small piece of sodium. **Result:**—

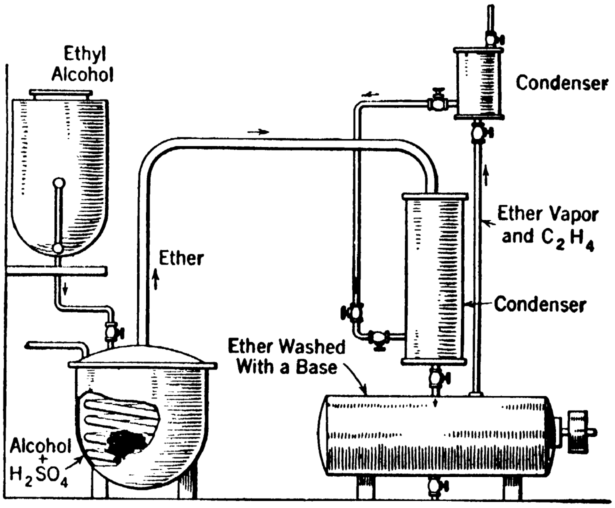

Fig. 35.—Manufacture of Ether.

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EXPT. 14. ETHER

1. What causes the heat of reaction when the H_2SO_4 is added to the alcohol?

2. Why is a sand bath used in Fig. 34?

   What else could you use in place of it?

3. Why is a long piece of rubber tubing attached to the side-arm of the suction flask in the apparatus?

4. Write the equation for the reaction between ethyl alcohol and H_2SO_4 at about 100°.

5. Write the equation for the reaction between ethyl acid sulfate and ethyl alcohol at about 140°.

6. What compound would be formed if the temperature were increased? Write the equation for this reaction.

7. What name is given to the method of preparation of ether as given in this experiment?

8. What impurities are present in the distillate?

9. Why is the ether, as prepared, washed with NaOH solution?

10. Why is the ether, as prepared, washed with a saturated solution of NaCl instead of water?

11. Why is there a cooling effect when ether evaporates from your hand?

12. Mention several uses for ether as a solvent.

13. What impurities are usually present in commercial ether?

How are they removed?

14. Compare the respective parts of the equipment in Fig. 35 with those shown in Fig. 34.

15. Why is a coil-heating device used in the still of Fig. 35?

16. What chemical tests will distinguish ethyl ether from its isomer, butyl alcohol?

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EXPT. 15. FORMALDEHYDE

Preparation.

1.—Refer to Expt. (*f*) (p. 51).

2.—To 1 cc. of methanol add a small crystal of potassium dichromate and 5 cc. of dilute sulfuric acid (1 : 5), and heat gently. Note the odor.

Properties.

NOTE.—In making the tests outlined below, formalin is used. This is a 35–40 per cent solution of formaldehyde in water, with the addition of a small amount of methanol to serve as a stabilizer.

(*a*) **Odor.**—Note the odor of formalin.

(*b*) **Removal of Water.**—Pour 1 cc. of formalin into a test tube. Add to it 3 or 4 small lumps of quicklime and warm gently until the reaction begins. Waft the fumes toward the nose. Note the odor. **Result:—**

(*c*) **Color Test with Resorcinol.**—See Expt. (*f*) (p. 51). **Result:—**

(*d*) **Casein Test.**—Slowly heat to boiling in a porcelain evaporating dish on an asbestos pad 5 cc. of milk, 5 cc. of conc. HCl which contains a minute quantity of a 0.5 per cent ferric chloride solution, and a trace of formalin. This should be stirred occasionally. A violet coloration, varying in intensity with the amount of formaldehyde present, is produced. If formaldehyde is not added the solution slowly turns brown. To remove any doubt regarding a positive test, a blank (i.e., repetition of the experiment without the formaldehyde) should be conducted.

(*e*) **Polymerization.**—Place 5 cc. of formalin on a watch glass and evaporate to dryness on a steam bath. **Result:—**

Place some of the residue on a crucible cover and heat. Note the odor.

(*f*) **Hardening Action of Formaldehyde.**—Put a part of the white of an egg and a piece of gelatin into a small beaker and cover with formalin. Allow to stand for an hour and note the hardening effect. Then try the action of boiling water on the products and also on some of the materials which have not been treated with formalin. **Results:—**

(*g*) **Silver Mirror Test.**—Use a test tube cleaned by boiling in strong NaOH solution and then rinsed well with distilled water. Introduce 3 cc. of a silver nitrate solution (10 per cent) into the tube and add a very dilute solution of ammonia (5 per cent), drop by drop, until the precipitate, which is formed at first just dissolves (avoid an excess of ammonia). Then add 5 drops of formalin and place the tube in a beaker of warm water for a few minutes, until a good silvering is produced. **Warning:** After the silver mirror is produced, discard the solution and wash test tube. (Explosive compound is produced in the solution on standing.)

(*h*) **Formaldehyde and Schiff's Reagent.**—To 3 cc. of Schiff's reagent add a drop of formalin. **Result:—**

(*i*) **Formaldehyde and Alkalies.**—Boil for 5 minutes in a water bath 5 cc. of formalin with 3 cc. of a strong solution of cold NaOH (40 per cent). **Result:—**

(*j*) **Hexamethylenetetramine.**—Pour 5 cc. of formalin and 5 cc. of ammonium hydroxide into an evaporating dish and evaporate to dryness on a steam bath. **Result:—**

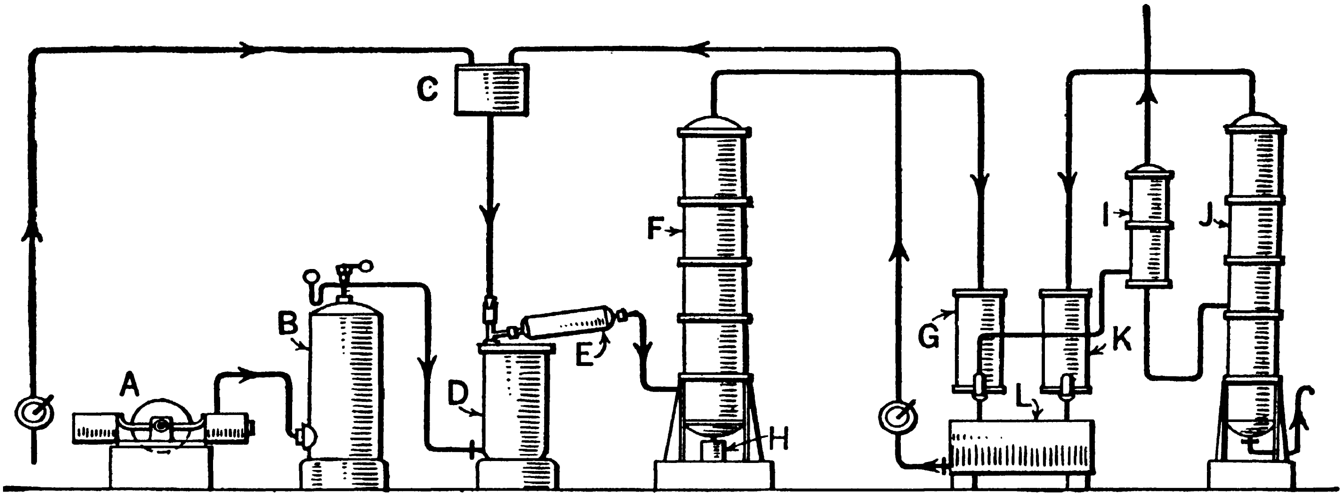

Fig. 36.—Manufacture of Formaldehyde.

A—Pump.
B—Compressed Air.
C—Methanol.
D—Mixing Tank.
E—Catalyst (Copper).
F—Condenser.
H—Receiver for Formaldehyde Solution.
G, K, I, J—Condensers.
L—Methanol Recovery Tank.

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EXPT. 15. FORMALDEHYDE

1. Write the equations for the preparation of formaldehyde as given in Method No. 1.

2. Write the equations for the preparation of formaldehyde as given in Method No. 2.

3. What compounds would be formed upon further oxidation of formaldehyde?

4. What is meant by the term "stabilizer"?

5. What is the function of the quicklime in Expt. (*b*)?

6. Outline the method used to prove that a sample of milk contains formaldehyde as a preservative.

   Is the use of formaldehyde permitted as a food preservative? Give reason.

7. What is the name of the product formed in Expt. (*e*)?
   What formula is ascribed to it?
   What use is made of this product in sanitation?

8. What is the general effect of formalin on protein-like products?

What industry makes practical use of this reaction?

9. Explain the reactions involved in Expt. (*g*).

What industry makes practical use of this reaction?

10. Write the equation for the formation of hexamethylenetetramine.

11. Discuss the steps in the manufacture of formaldehyde as shown in Fig. 36.

12. What is the composition of formalin?

13. Give uses for formaldehyde.

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PREPARATION OF AN ALDEHYDE (METHOD NO. 1)

EXPT. 16. ACETALDEHYDE

Warning:—*Acetaldehyde is very volatile (b.p. 20.8°). Keep it well stoppered when not in use.*

Preparation.

Method No. 1.—Grind together in a mortar 10 g. of fused calcium acetate and 10 g. of sodium formate. Transfer the mixture to a 20 cm. hard-glass test tube and arrange the apparatus as shown in Fig. 37.

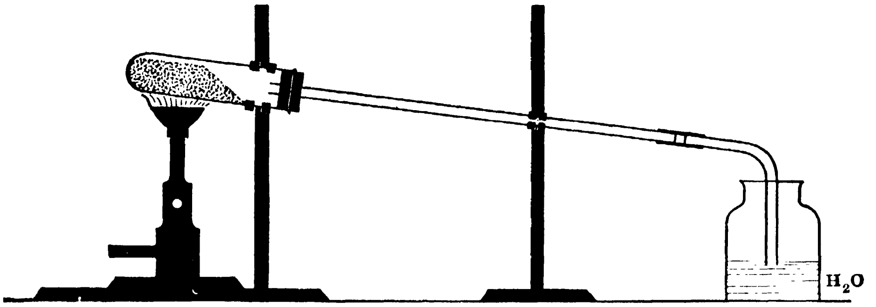

FIG. 37.

Heat and collect the product in water. It contains acetaldehyde. Perform the silver mirror test as in Expt. (*g*) (p. 63). **Result:**—

Method, No. 2.—Arrange the apparatus as shown in Fig. 38. Introduce 40 cc. of paraldehyde into the flask. Add 2 cc. of 20 per cent H_2SO_4, shake and distill from a hot water bath, the temperature of which is kept at approximately 80°. Acetaldehyde boils at 20.8°. Perform the Schiff test as in Expt. (*h*) (p. 63). **Result:**—

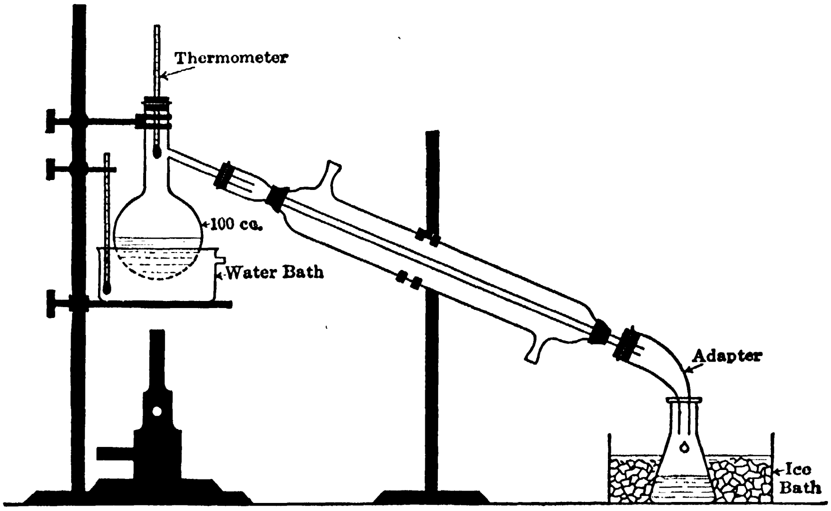

FIG. 38.

Properties.

Note.—Use the acetaldehyde obtained from the stock room or prepare it according to Method No. 2 given above.

(*a*) **Odor.**—Note the odor of acetaldehyde. Compare it with that of formaldehyde.

(*b*) **Silver Mirror Test.**—Perform according to Expt. (*g*) (p. 63). **Result:—**

(*c*) **Test with Fehling's Solution.**—Add 2 drops of acetaldehyde to 5 cc. of Fehling's solution and warm gently. **Result:—**

(*d*) **Schiff's Test.**—Add 2 drops of acetaldehyde to 5 cc. of Schiff's reagent. **Result:—**

Heat 3 cc. of Schiff's reagent alone. **Result:—**

(*e*) **Acetaldehyde and Sodium Bisulfite.**—Saturate about 25 cc. of water with $NaHSO_3$ and SO_2 gas at room temperature. Filter. Pour 5 cc. of the filtrate into each of two dry test tubes. To one add 3 cc. of acetaldehyde in 1 cc. portions. Cool and shake after each addition. In about an hour examine the contents of both test tubes. **Results:—**

(*f*) **Acetaldehyde and Phenylhydrazine.**—Dissolve 1 g. of phenylhydrazine hydrochloride and 2.5 g. of sodium acetate in 10 cc. of water. Filter and add 10 drops of acetaldehyde. Shake and warm for 20 minutes in a water bath. **Result:—**

Immerse the test tube in a bath of an ice-salt mixture for about an hour. **Result:—**

(*g*) **Oxidation of Acetaldehyde.**—To 3 cc. of potassium dichromate solution (10 per cent) and 3 cc. of dilute H_2SO_4 (10 per cent) add 1 cc. of acetaldehyde and heat gently. **Result:—**

Hold a piece of blue litmus paper in the vapors coming from the tube. **Result:—**

(*h*) **Acetaldehyde and Strong NaOH Solution.**—Perform as in Expt. (*i*) (p. 63). **Result:—**

(*i*) **Polymerization.**—To 1 cc. of acetaldehyde add *1 drop* of conc. H_2SO_4. Shake. Paraldehyde is the product formed.

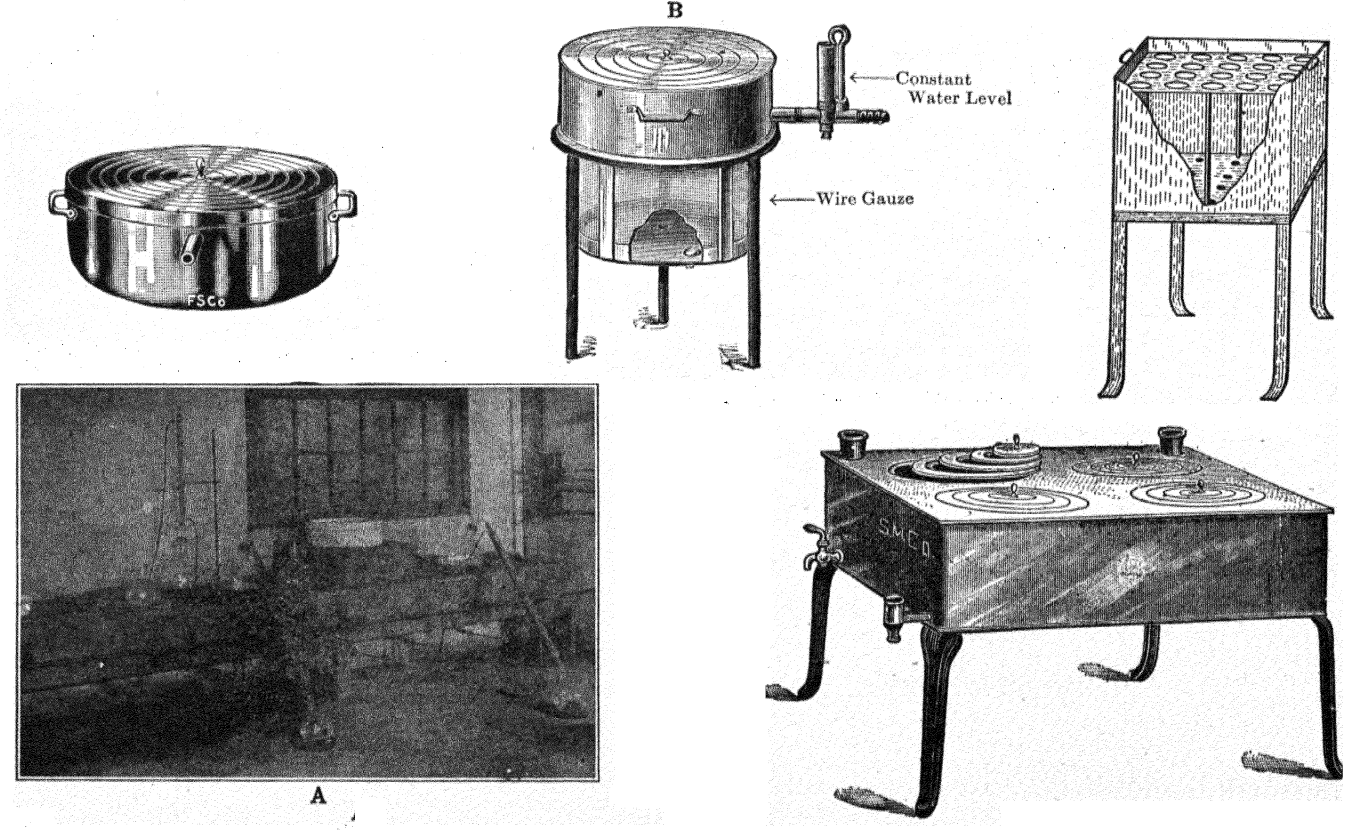

Fig. 39.—Water Baths.

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EXPT. 16. ACETALDEHYDE

1. Write the equation for the formation of acetaldehyde as given in Method No. 1.

2. Write the equation for the type reaction for the preparation of aldehydes by this method.

3. Why is the acetaldehyde collected in a bottle of water in Method No. 1?

4. Why is the acetaldehyde prepared in Method No. 2 collected in a bottle surrounded by ice?

5. Explain the reactions involved in Expt. (*c*)?

6. What happens when Schiff's reagent is heated?

7. Write the equation for the reaction involved in Expt. (*e*).

8. Write the equation for the reaction involved in Expt. (*f*).

9. Why is sodium acetate used in Expt. (*f*)?

10. What acid is produced in Expt. (*g*)?

11. Compare the result of Expt. (*h*) with the result of the analogous experiment under formaldehyde.

12. What is the graphic formula for paraldehyde as formed in Expt. (*i*)?

13. Would pure paraldehyde respond to the acetaldehyde reactions? Give reason.

14. Tabulate the equations of formaldehyde and acetaldehyde with the various reagents used on page 68.

15. What is the reason for enclosing the flame with a wire gauze in the water bath shown in Fig. 39B? Explain the principle involved.

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PREPARATION OF A KETONE

EXPT. 17. ACETONE

Preparation.

Put 20 g. of finely pulverized anhydrous calcium acetate in a 20 cm. hard-glass test tube. Arrange the apparatus as shown in Fig. 40.

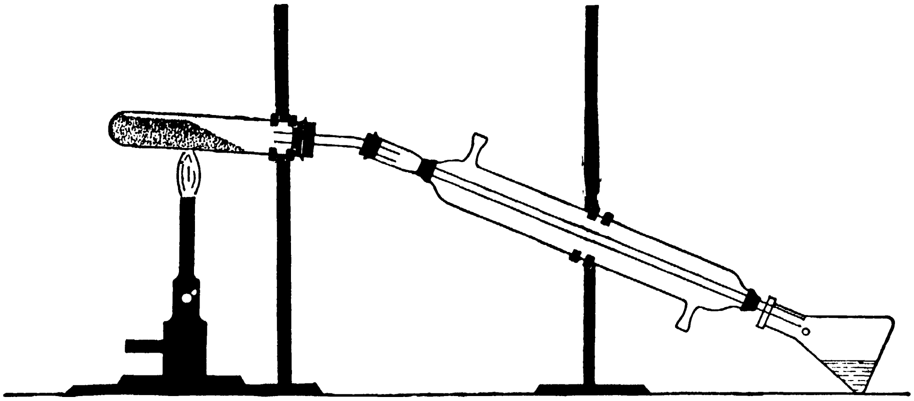

FIG. 40.

Heat until no more material distills over. The tarry matter in the distillate is removed by shaking with an equal volume of water, which dissolves the acetone. Filter through a fluted filter paper. Pour the filtrate into a small flask, add about 10 g. of quicklime, attach a reflux condenser and after the reaction has subsided replace the condenser with a cork stopper. Allow to stand until the next laboratory period. Distill the acetone from the lime on a water bath. The acetone may be further dried by allowing the liquid from the lime to stand in contact with anhydrous $CaCl_2$ for several hours. Distill from a water bath and collect the fraction distilling between 55°–56°.

Properties.

(Use the acetone obtained from the stock room.)

(*a*) **Color.**—Note the color of acetone.

(*b*) **Odor.**—Note the odor of acetone.

(*c*) **Flammability.**—Dip a glass rod into some acetone and hold it in the flame. **Result:**—

(*d*) **Solubility in Water.**—Add 3 cc. of acetone to 3 cc. of water and shake. **Result:**—

Add 2 g. of solid NaCl and shake. **Result:**—

(*e*) **Separation of Acetone from Aqueous Solution.**—To 5 cc. of acetone add 5 cc. of water and shake. Then add solid NaOH to the solution until it is saturated. **Result:**—

(*f*) **Silver Mirror Test.**—Perform according to Expt. (*g*) (p. 63). **Result:**—

(*g*) **Test with Fehling's Solution.**—Perform according to Expt. (*c*) (p. 68). **Result:**—

(*h*) **Schiff's Test.**—Perform according to Expt. (*h*) (p. 63). **Result:**—

(*i*) **Acetone and Sodium Bisulfite.**—Gradually add with constant stirring 12 g. of $NaHSO_3$ to 15 cc. of ike-warm water. Continue stirring for 3 minutes after all the bisulfite has been added. Allow to cool to room temperature, pass in SO_2 gas and filter. Cool the filtrate in ice water. Add gradually and with constant stirring 7 cc. of acetone. **Result:**—

To about one-third of the above mixture add 10 cc. of Na_2CO_3 solution (10 per cent) and heat. **Result:**—

Note the odor:—

(*j*) **Acetone and Phenylhydrazine.**—Dissolve 1 g. of phenylhydrazine hydrochloride and 2.5 g. of sodium acetate in 10 cc. of water. Filter and add 10 drops of acetone. Shake and warm for 20 minutes in a water bath. **Result:**—

Immerse the test tube in an ice bath for about an hour. **Result:**—

(*k*) **Iodoform Test.**—Perform according to Expt. (*k*) (p. 56). **Result:**—

(*l*) **Acetone and Strong NaOH Solution.**—Repeat Expt. (*i*) (p. 63). **Result:**—

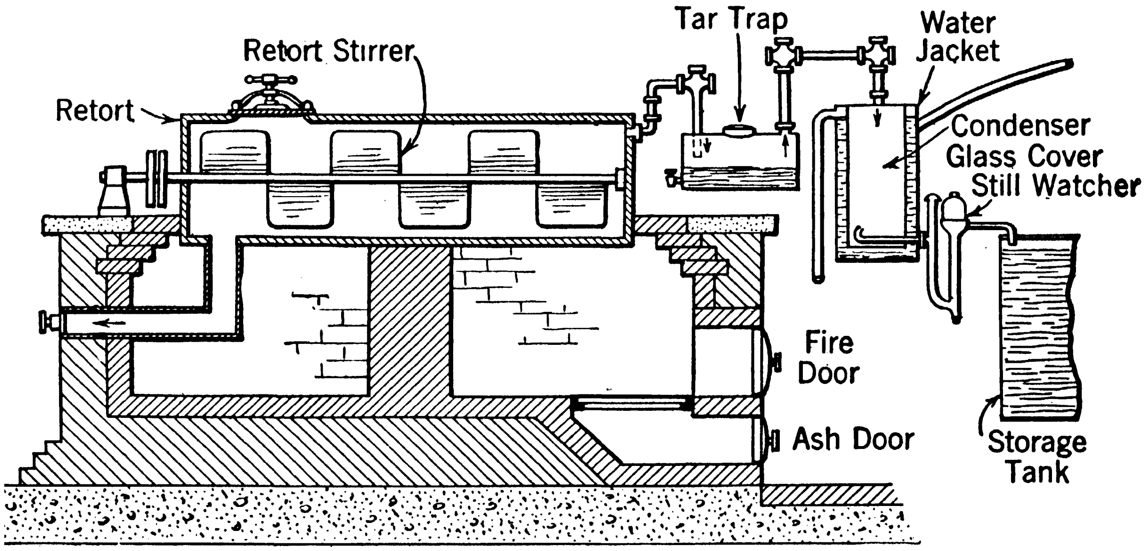

Fig. 41.—Diagram of Acetone Plant.

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EXPT 17. ACETONE

1. Write the equation for the preparation of acetone from calcium acetate.

2. Write the equation for the type reaction for the preparation of ketones by this method.

3. What is the advantage in using a fluted filter paper?

4. What compound does the quicklime remove?

5. What is the function of the solid NaOH in Expt. (*e*)?

6. Neatly tabulate the action of acetone and acetaldehyde with the following reagents:—
(*a*) ammoniacal $AgNO_3$ solution, (*b*) Fehling's solution, (*c*) Schiff's reagent, (*d*) sodium bisulfite, (*e*) phenylhydrazine and (*f*) strong NaOH solution.

Which reagents would you use in order to differentiate between aldehydes and ketones?

7. Write the equations for the reactions in Expt. (*i*).

8. Write the equation for the reaction in Expt. (*j*).

9. What compounds thus far tested give the iodoform test?

10. What substance is used commercially for the preparation of acetone?

11. Describe the commercial preparation of acetone using Fig. 41 as a basis.

12. Give uses for acetone.

13. What are the present industrial sources of acetone?

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EXPT. 18. FORMIC ACID

Properties.

Warning:—*Do not allow formic acid to come in contact with the skin.*

(*a*) **Odor.**—Note the odor of formic acid.

(*b*) **Test with Litmus Papers.**—To 5 cc. of water add 3 drops of formic acid; shake, and test with litmus papers. **Result:**—

(*c*) **Action of H_2SO_4 on Formic Acid.**—To 2 cc. of formic acid add, a few drops at a time, 3 cc. of conc. H_2SO_4 and heat gently. (Do not breathe the gas evolved nor allow it to escape into the room.) Hold a flame to the mouth of the test tube. Note the color of the flame produced by the burning gas.

(*d*) **Oxidation of Formic Acid.**—To 5 cc. of formic acid add 2 cc. of dilute H_2SO_4 (10 per cent) and add a few crystals of $KMnO_4$ and shake. **Result:**—

Test the evolved gas by passing it into clear lime-water. **Result:**—

(*e*) **Reducing Action of Formic Acid.**—Into each of two test tubes pour 5 cc. of a 20 per cent solution of sodium formate. To one tube add 2 cc. of a 10 per cent solution of $AgNO_3$, to the other 2 cc. of a 10 per cent solution of mercuric chloride. Heat both tubes. **Results:**—

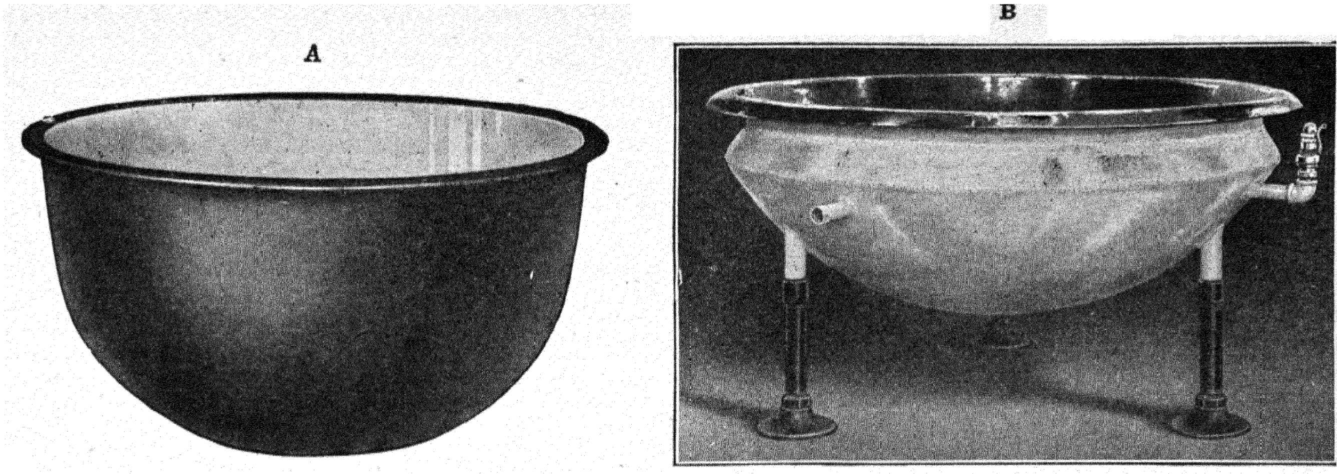
(*f*) **Salts of Formic Acid.**—1. To 2 g. of lead oxide (litharge) add 10 cc. of formic acid. Heat gently for about 5 minutes, filter and set the hot solution aside to crystallize. **Result:**—

2 Repeat Expt. 1 using cupric oxide instead of lead oxide. **Result:**—

3. Neutralize 2 cc. of formic acid with dilute NaOH solution (10 per cent), using litmus paper as an indicator. Evaporate the solution to dryness on a water bath. **Result:**—

(*g*) **Action of Heat on a Formate.**—In a dry test tube fuse 2 g. of dry sodium formate. Test the gas evolved by holding a lighted match at the opening of the tube. **Result:**—

Dissolve the residue in the test tube in water. Filter and make the filtrate slightly ammoniacal. Add $CaCl_2$ solution (10 per cent). **Result:**—



Steam Jacketed and Glass-lined.

Fig. 42.—Evaporating Pans.

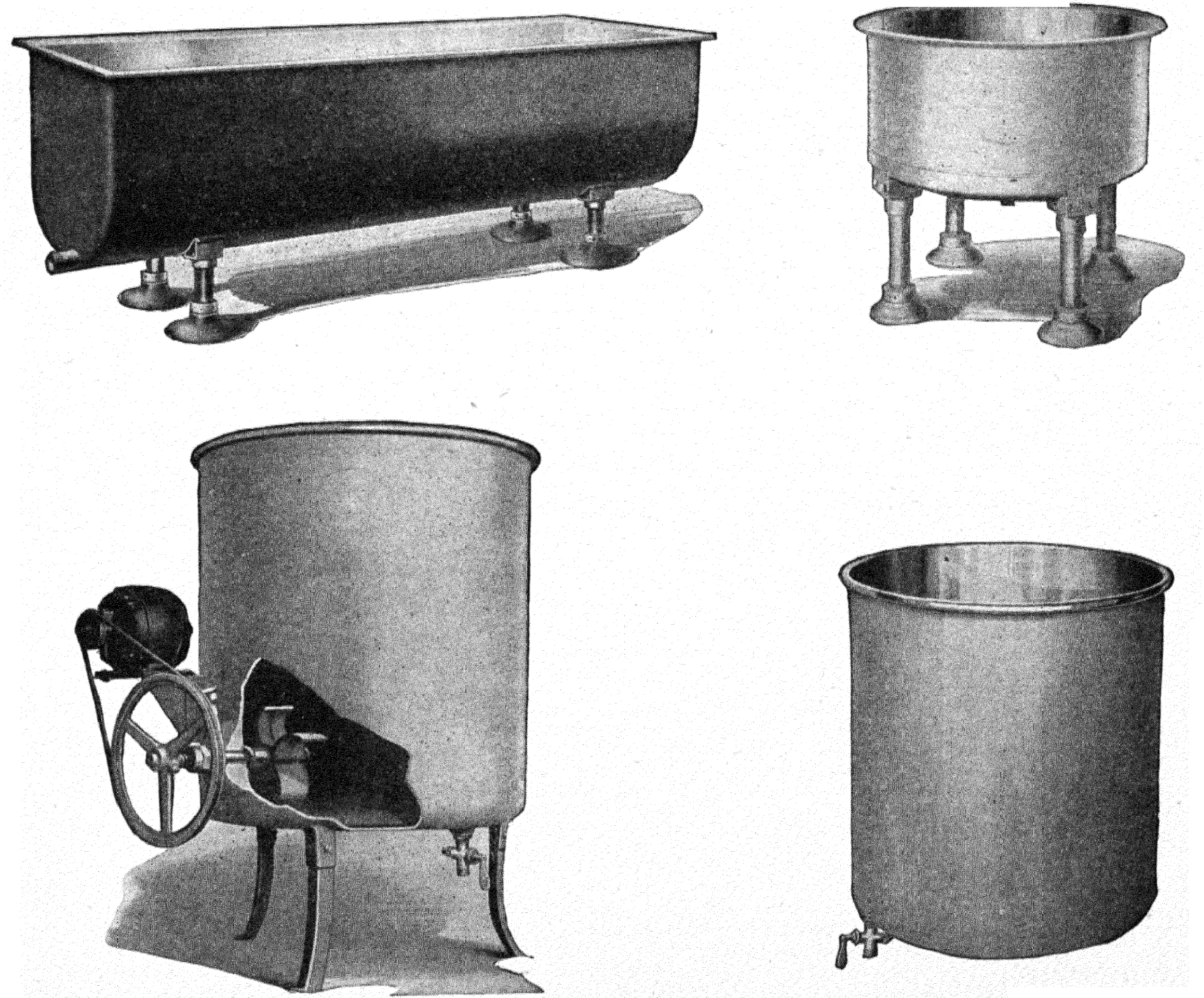


Fig. 43.—Glass-lined Chemical Equipment.

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EXPT. 18. FORMIC ACID

1. Write the equations for the reactions in Expt. (*c*).

2. Write the graphic formula for formic acid.

   What grouping in formic acid renders it susceptible to oxidation as shown in Expts. (*d*) and (*e*)?

3. Write the equations for the reactions in Expt. (*d*).

4. Write the equations for the reactions in Expt. (*e*).

5. Write the formulas for the compounds prepared in Expt. (*f*).

6. Write the equations for the reactions involved in Expt. (*g*).

7. Is CO the anhydride of formic acid? Give reason.

8. What is the effect of formic acid on the skin?

9. What treatment would you apply if formic acid came in contact with your skin?

10. Give two methods for the preparation of formic acid. Which is the commercial method?

11. What are the advantages of glass-lined chemical equipment?

With what materials is its use unsuitable?

What is a disadvantage in the use of glass-lined equipment?

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PREPARATION OF AN ACID FROM A SALT

EXPT. 19. ACETIC ACID

Preparation.

Into a dry 200 cc. distilling flask put 75 g. of pulverized fused sodium acetate. (Prepare the fused salt, see p. 25.) Add, in portions of 5 cc., 40 cc. of conc. H_2SO_4. Shake after each addition. Arrange the apparatus as shown in Fig. 8 (p. 19) and collect that portion of the distillate which boils between 118°–120°. Pure acetic acid boils at 119°.

Yield = g. Calculated = g. Percentage Yield =

Properties.

(*a*) **Odor.**—Note the odor of acetic acid.

(*b*) **Solubility in Water.** To 5 cc. of water add 5 drops of acetic acid and shake. **Result:—**

(*c*) **Flammability.**—Pour 2 cc. of acetic acid on to a watch glass and apply a lighted match. **Result:—**

Now place 2 cc. in a test tube, heat and hold a lighted match to the vapors. **Result:—**

(*d*) **Freezing-point of Acetic Acid.**—Surround a test tube containing 5 cc. of acetic acid with cracked ice. Stir with a thermometer and note the temperature of solidification. Pure acetic acid melts at 16.7°.

(*e*) **Cacodyl Oxide Test for Acetic Acid.**—(HOOD.)—**Warning:**—Since cacodyl oxide is very poisonous, be very careful in carrying out this experiment. Discontinue the heating as soon as the odor is detected.

Heat 0.5 g. of anhydrous sodium acetate with 0.5 g. of arsenious oxide. Note the odor by wafting the vapors toward the nose. **Result:—**

(*f*) **Ethyl Acetate Test.**—Repeat Expt. (*l*) (p. 56). **Result:—**

(*g*) **Basic Ferric Acetate Formation.**—Neutralize 1 cc. of acetic acid with a 5 per cent solution of NaOH. Use litmus paper to indicate the neutral point. Add 1 cc. of a 10 per cent solution of ferric chloride. Boil and set aside to allow the precipitate to settle. **Result:—**

(*h*) **Vinegar.**—Vinegar contains 4–6 per cent of acetic acid.

1. **Odor.**—Note the odor of vinegar.

2. **Taste.**—Note the taste of vinegar.

3. **Litmus.**—Test some vinegar with litmus papers. **Result:—**

4. **Presence of inorganic substances.**—Place 20 cc. of vinegar in a small porcelain dish and evaporate to dryness on a water bath. Note the residue. Then place the dish on a clay triangle and ignite. Test the ash produced for carbonates, sulfates, phosphates and halides. **Results:—**

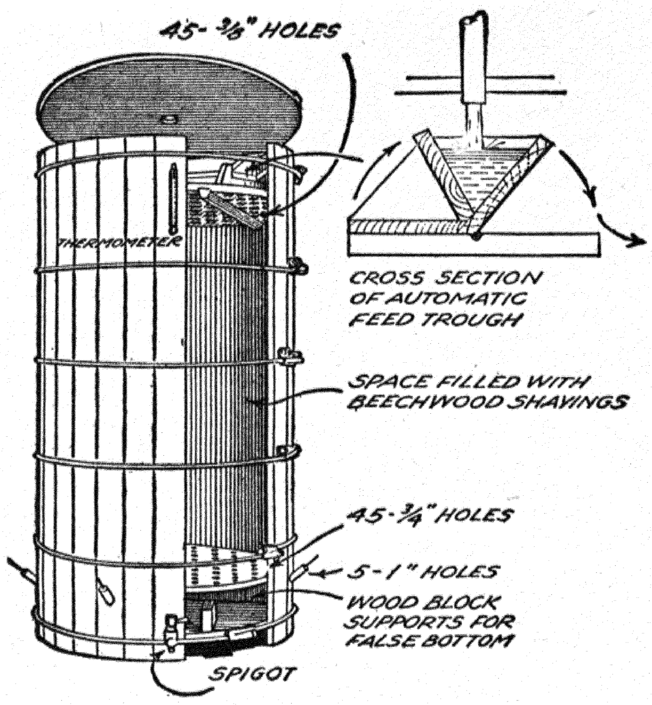

Fig. 44.—Vinegar Generator for "Quick" or Generator Process.

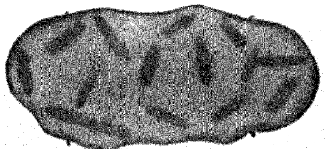

Fig. 45.—Acetic Acid Bacteria.

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EXPT. 19. ACETIC ACID

1. Write the equation for the preparation of acetic acid as performed in this experiment.

2. What compound would result if the fused sodium acetate were heated too strongly?

3. Why is concentrated acetic acid called glacial acetic acid? See Expt. (*d*).

4. Write the equation for the reaction in Expt. (*e*).

5. Write the equation for the reaction in Expt. (*f*). What is the function of the H_2SO_4?

6. Write the equations for the reactions in Expt. (*g*).

7. What classes of substances are present in vinegar besides acids?

8. What are the sources of the following: (*a*) white vinegar, (*b*) cider vinegar, and (*c*) malt vinegar?

9. What is the source of commercial acetic acid?

10. Describe in detail the "quick" vinegar process, the diagram for which is given in Fig. 44.

11. Give the uses of acetic acid.

12. Name several important salts of acetic acid and give their uses.

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EXPT. 20. SOAP—GLYCEROL—FATTY ACIDS

(Use distilled water)

Preparation.

Put 10 g. of lard in a porcelain evaporating dish and add, with constant stirring, a solution of 10 g. of NaOH in 10 cc. of water. Stir 5 minutes longer. Heat on a water bath for 1 hour with frequent stirring. Add water occasionally to replace that which has boiled off. Allow to cool. Add 30 cc. of water, stir thoroughly and break up the granules. Filter the entire mass through a piece of muslin until nearly all of the liquid has passed through the cloth; then press out the remainder of the liquid. Save the filtrate for Expt. (*g*).

To 2 g. of the prepared soap add just enough water to dissolve it. Filter. Saturate the filtrate with NaCl. Set aside for 15 minutes and then skim off the soap.

Properties.

(*a*) **Test for Free Alkali in Soaps.**—Place small pieces (size of a pea) of your prepared soap, laundry soap and ivory soap in three dry test tubes. Add 10 cc. of alcohol to each and shake. Add 2 drops of phenolphthalein solution to each and shake. **Results:—**

(*b*) **Hydrolysis of Soap.**—Dissolve a small piece of Ivory soap by shaking it vigorously with 10 cc. of cold water. Filter and add 2 drops of phenolphthalein solution. **Result:—**

(*c*) **Soap as an Emulsifying Agent.**—Shake 4 drops of cottonseed oil with 10 cc. of water. **Result:—**

Allow to stand for a period of 10 minutes. **Result:—**

Now add 1 cc. of a filtered Ivory soap solution and shake. **Result:—**

Allow it to stand again for 10 minutes. **Result:—**

(*d*) **Water in Soap.**—Place a few shavings of Ivory soap in a test tube. Heat gently. **Result:—**

(*e*) **Free Fat in Soap.**—To a few shavings of toilet soap add 15 cc. of ether. Shake and filter. Pour the filtrate on a watch glass and allow it to evaporate under the hood. **Result:—**

(*f*) **Hardness in Water.**—1. To 15 cc. of distilled water add 2 cc. of a filtered saturated Ivory soap solution and shake. **Result:—**

2. Repeat with tap water instead of distilled water. **Result:—**

3. Repeat Expt. 1 and add 2 cc. of a 10 per cent solution of $CaCl_2$. **Result:—**

4. Repeat Expt. 1 and add 2 cc. of a 10 per cent solution of $MgSO_4$. **Result:—**

5. Repeat Expt. 1 and add 2 cc. of a 10 per cent solution of $FeSO_4$. **Result:—**

(*g*) **Separation and Test for Glycerol.**—Take the filtrate which you obtained in the preparation of soap and neutralize it with HCl (10 per cent). Filter, and evaporate the filtrate to dryness on a water bath. Extract the solid residue with 30 cc. of hot alcohol. Filter the alcoholic extract and evaporate on a steam bath. The residue contains glycerol.

Tests for Glycerol.—1. Acrolein test: To a portion of the impure glycerol obtained above add 0.5 g. of pulverized fused $KHSO_4$, mix thoroughly and heat strongly. Note the odor. **Result:**—

2. Borax bead test: Make a small loop on the end of a platinum wire. Dip the loop into some borax and heat strongly in the flame. Allow it to cool, dip the bead into the glycerol residue, and hold it in the edge of the flame. Observe the green color of the flame immediately after inserting the bead.

(*h*) **Fatty Acids from Soap.**—Dissolve 2 g. of the prepared soap in water, filter, and to the filtrate add 20 cc. of HCl (10 per cent), and filter again. Try the solubility of the precipitate in water and in ether. **Results:**—

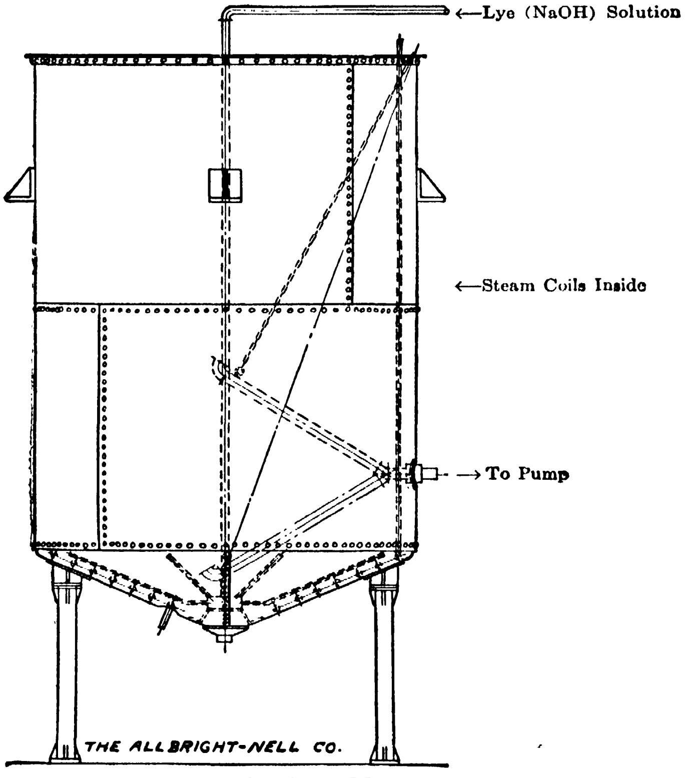

FIG. 46.—Kettle for Soap Manufacture.

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EXPT. 20. SOAP—GLYCEROL—FATTY ACIDS

1. Write the general type formula for fats and vegetable oils.

2. Write the general equation showing the action of alkalies on fats and vegetable oils and name the products formed.

What is this type of reaction called?

3. Explain the theory for the addition of NaCl in the salting out of soap.

4. Why do you use alkaline materials to remove fatty substances from your hands?

5. What alkali would you use to make soft soap?

6. For what purpose are the soaps containing free alkali used in the household? Why?

7. Explain the hydrolysis of soap as given in Expt. (*b*) and write the equation.

8. In what industry is emulsification with soap important?

9. Why should one not buy a large quantity of soap merely on the basis of weight?

10. Is the presence of free fat in soap objectionable? Give reason.

11. The ions of what elements produce hardness in water?

12. Write the equations for the reactions in Expt. (*f*).

13. Why do you neutralize the solution in Expt. (*g*).

14. What is the function of the $KHSO_4$ in Expt. (*g*) (1)?

To what compound is the odor due?

15. Name the important fatty acids that are precipitated in Expt. (*h*).

16. Discuss the theory of the detergent action of soaps.

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PREPARATION OF AN ESTER

EXPT. 21. ETHYL ACETATE

Preparation.

Pour 50 cc. of ethyl alcohol into the distilling flask and add in small portions, with constant shaking, 50 cc. of conc. H_2SO_4. Cool if boiling occurs. Arrange the apparatus as shown in Fig. 47. Heat the mixture to 140° on an oil bath (thermometer in the bath). When this temperature is reached, drop into the flask through the dropping funnel a mixture of 100 cc. of alcohol and 100 cc. of glacial acetic acid. This mixture is added at the same rate at which the ethyl acetate distills over. When all the alcohol-acetic acid mixture has been added, continue the distillation for 15 minutes longer. In order to purify the ethyl acetate, transfer it to a separatory funnel and shake it with half its volume of a 15 per cent solution of Na_2CO_3. If the upper layer shows an acid reaction with litmus paper add more of the carbonate solution, shake and allow to separate. Discard the lower layer. Now shake the ethyl acetate in the dropping funnel with a solution of 40 g. of $CaCl_2$ in 40 cc. of water. Allow to separate and discard the lower layer. Repeat this washing with another solution of $CaCl_2$ of the same concentration. Transfer the upper layer to an Erlenmeyer flask, add 2 g. of anhydrous $CaCl_2$ and allow to stand until the next laboratory period. Filter the supernatant liquid into a 200 cc. distilling flask and distill from a water bath. Collect the fraction distilling over between 72°–77°. The boiling point of ethyl acetate is 77°.

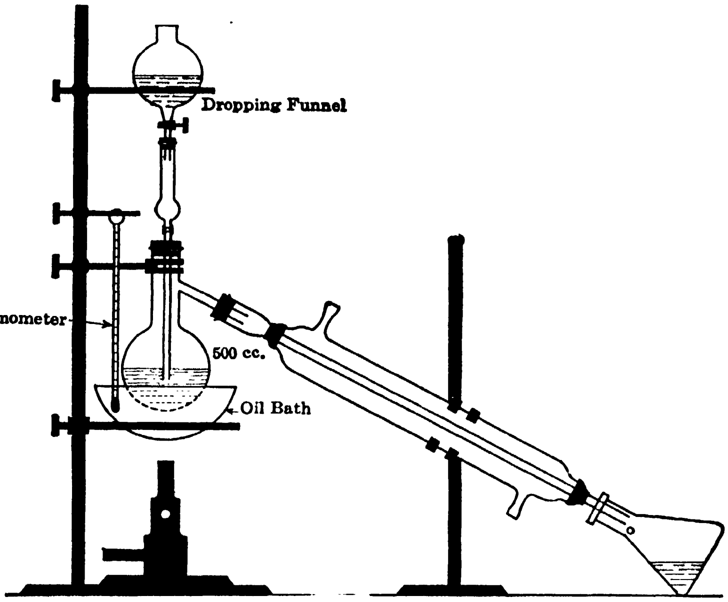

Fig. 47.

Yield =   g.   Calculated from the acetic acid used =   g.   Percentage yield =

Properties.

(a) **Odor.**—Note the odor of ethyl acetate.

(b) **Hydrolysis of Ethyl Acetate.**—Pour 20 cc. of the ethyl acetate which you prepared into a 100 cc. flask. Add 50 cc. of a 10 per cent solution of NaOH. Connect the flask to a reflux condenser and heat over an asbestos pad for 1 hour. At the end of this time distill over 15 cc. of liquid. Saturate the distillate with K_2CO_3, i.e., add it until no more dissolves. Two layers will appear. Separate the upper layer (alcohol) and apply the iodoform test. **Result:**—

To the solution remaining in the distilling flask add dilute H_2SO_4 (10 per cent) until it shows a decidedly acid reaction. Distill over 15 cc. heating on a wire gauze. Test for acetic acid as in Expt. (*g*) (p. 79). **Result:**—

(*c*) **Solvent Action.**—Add 10 cc. of ethyl acetate to about 0.2 g. of cellulose acetate. **Result:**—

(*d*) **Miscellaneous Esters.**—Note the odor of the following: (*a*) isoamyl acetate; (*b*) amyl butyrate (*c*) ethyl butyrate; (*d*) ethyl propionate; etc. **Results:**—

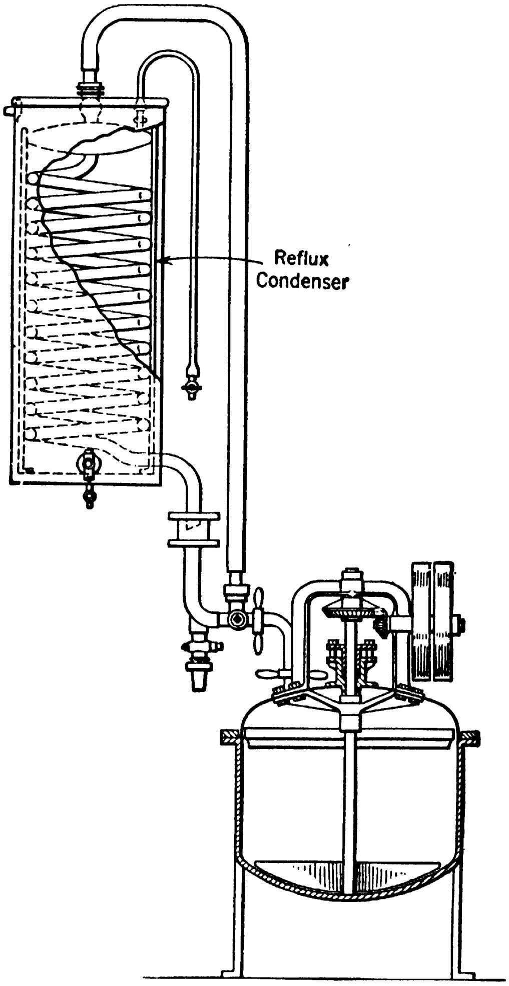

Fig. 48.—Still with Reflux Condenser.

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EXPT. 21. ETHYL ACETATE

1. Write the equation for the reaction taking place between ethyl alcohol and H_2SO_4 when heated.

2. Write the equation for the reaction between ethyl hydrogen sulfate and acetic acid at 140°.

3. What is the function of the H_2SO_4 in the preparation of ethyl acetate?

4. Why is the alcohol-acetic acid mixture added drop by drop?

5. Why is the distillate containing the ethyl acetate washed with sodium carbonate solution?

   What acids do you expect to be present in the distillate?

6. Why is the distillate washed with a concentrated $CaCl_2$ solution?

7. Write the equation for the type reaction used in this method of preparing an ester.

8. What is this type of reaction called?

9. What important industry uses ethyl acetate as a solvent?

10. Write the equation for the reaction involved in the hydrolysis of ethyl acetate as performed in this experiment.

11. What type of hydrolysis other than alkaline could be used?

12. What general name is applied to the type of reaction in Expt. (*b*)?

13. In what naturally occurring substances are many of these esters found?

What industries use these esters?

14. Why were esters formerly called "ethereal salts"?

15. Explain the terms (*a*) velocity of esterification and (*b*) rate of hydrolysis.

16. From a study of the industrial apparatus in Fig. 48, indicate the corresponding parts of the laboratory apparatus in Fig. 22.

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EXPT. 22. FATS AND OILS

Properties.

(*a*) **Solubility.**—Test the solubility of cottonseed oil in each of the following: cold alcohol, hot alcohol, ether, water, chloroform, benzene, carbon tetrachloride, gasoline, dilute acids and dilute alkalies. **Results:**—

(*b*) **Spotting Effect.**—Put a drop of olive oil on a piece of filter paper. On other parts of the same paper place a drop of alcohol and a drop of ether. After a few minutes note the appearance of the paper by holding it up to the light. **Results:**—

How would you remove this spot?

(*c*) **Emulsification.**—Refer to Expt. (*c*) (p. 83).

(*d*) **Reaction of Fresh Butter with Litmus.**—Shake a small lump of fresh sweet butter with alcohol. Test the solution with blue litmus paper. **Result:**—

(*e*) **Reaction of Rancid Butter with Litmus.**—Repeat Expt. (*d*) using rancid butter in place of fresh butter. **Result:**—

(*f*) **Saponification of Fats.**—Refer to the preparation of soap (Expt. 20) (p. 83).

(*g*) **Acrolein Formation.**—Place some lard on a crucible cover and heat strongly. Note the odor. **Result:**—

Also refer to Expt. (*g*) (1) (p. 84).

(*h*) **Test for Unsaturation.**—To 1 cc. of cottonseed oil add 5 cc. of ether and shake. To this solution add 3 drops of bromine and shake. **Result:**—

(*i*) **Exposure to Air.**—On a glass plate spread very thin films of olive oil, linseed oil, linseed oil containing a " drier," and lard. Set aside until the next laboratory period. **Results:**—

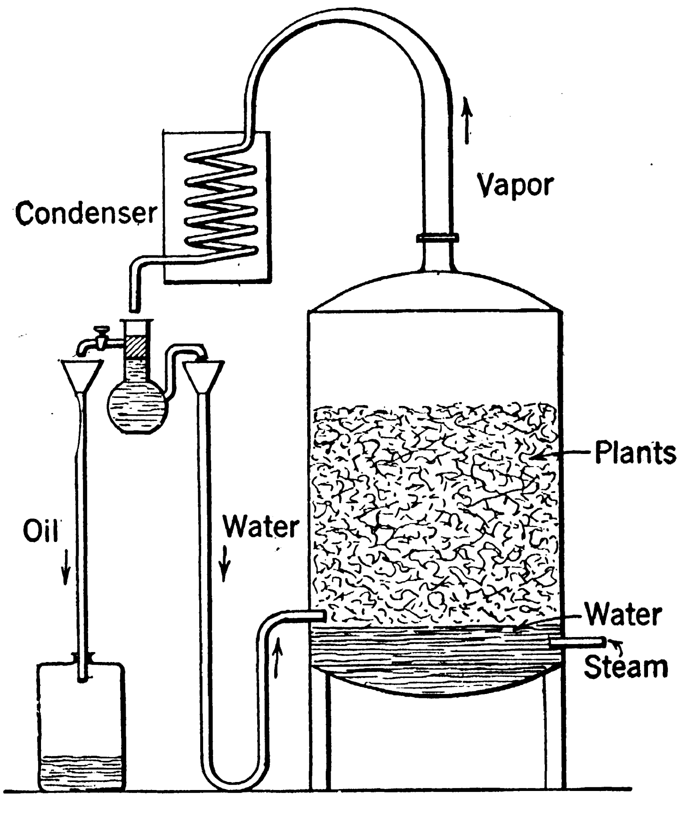

FIG. 49.—Extraction Apparatus.

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EXPT. 22. FATS AND OILS

1. To what class of organic compounds do fats and vegetable oils belong?

2. What chemical explanation is given to account for the differences in state and consistency of fats and vegetable oils?

3. Account for the formation of acids in rancid butter.

What produces this change?

4. Why can $Ca(OH)_2$ not be used in soap manufacture?

5. What is the source of acrolein in Expt. (*g*)?

6. What principal component in cottonseed oil responds to the bromine addition reaction in Expt. (*h*)?

7. Explain the principle of the drying of linseed oil in Expt. (*i*).

8. Name substances which may be added to linseed oil to hasten its drying on exposure to air.

9. Write the equation to show the hydrolysis of fats or oils with dilute H_2SO_4 and name the organic compounds produced.

10. Explain the term " hydrogenation of oils."

What important application is made of this process?

What is the chemistry of the process? Give the equation.

11. Describe in detail the extraction apparatus shown in Fig. 49.

12. Write the general type formula for fats.

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PREPARATION OF AN ACYL HALIDE

EXPT. 23. ACETYL CHLORIDE

Preparation.

Warning:—*Do not allow acetyl chloride or phosphorus trichloride to come in contact with the skin. Also be careful not to inhale any of the vapors.*

(Perform under the hood).

Put 75 g. of glacial acetic acid into the distilling flask. Arrange the apparatus as shown in Fig. 50, having cold water in the water bath. Then add through the separatory funnel, drop by drop, 60 g. of phosphorus trichloride. When all the phosphorus trichloride has been added, heat on the water bath, which is kept at a temperature of 40°–50°. Continue the heating until the liquid separates into two layers and until the evolution of HCl gas slackens. Now raise the temperature of the water bath and continue the heating until no more liquid distills over. Then distill the liquid from the receiver, using the same arrangement of apparatus as before, merely replacing the dropping funnel with a thermometer. Collect the fraction distilling between 50° and 58°. The boiling point of acetyl chloride is 55°. Transfer the product obtained to a glass-stoppered bottle and preserve for use in the following experiment.

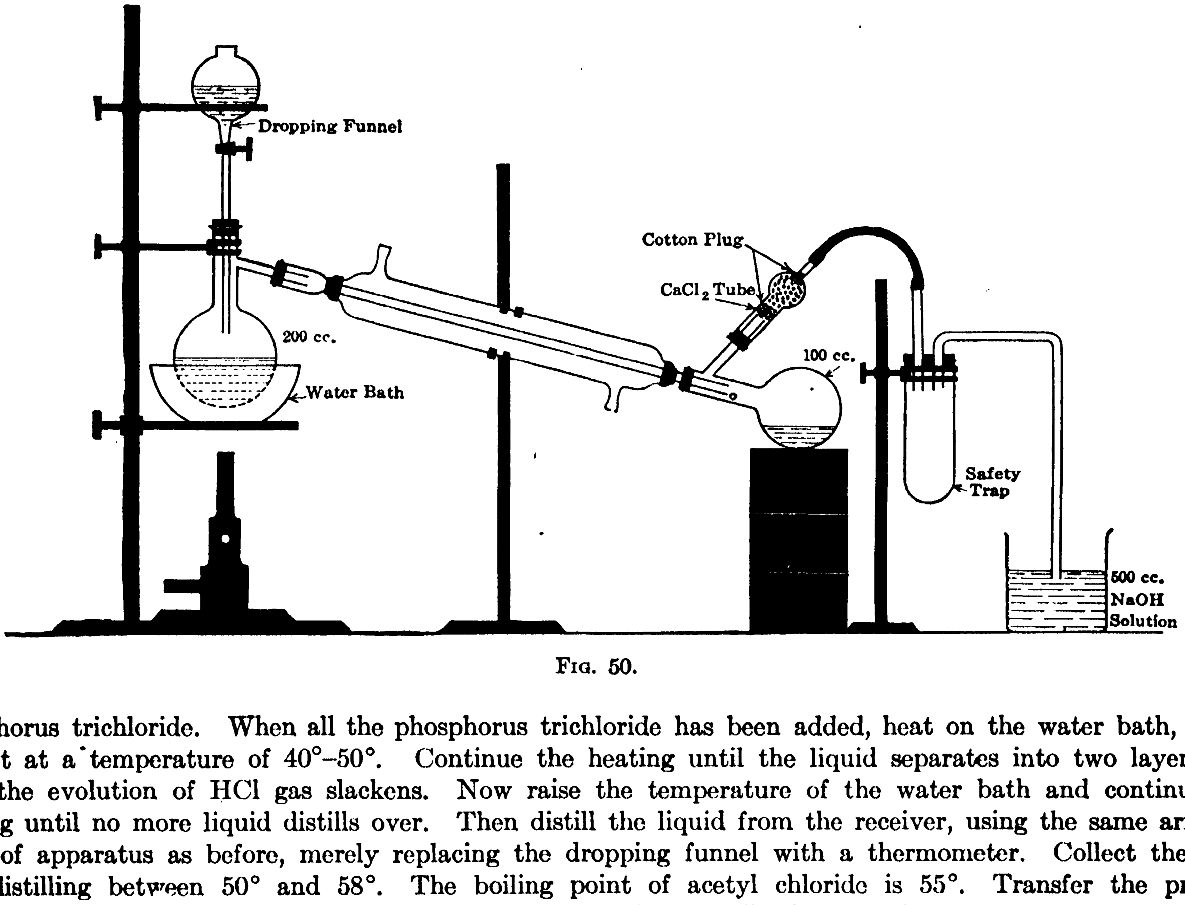


FIG. 50.

Yield = g. Calculated = g. Percentage yield =

Properties.

(*a*) **Action of Water.**—To 2 cc. of cold water add slowly 5 drops of acetyl chloride. Note **that the** acetyl chloride sinks to the bottom of the tube. Now shake and note the evolution of heat **and a gas. What is it?**

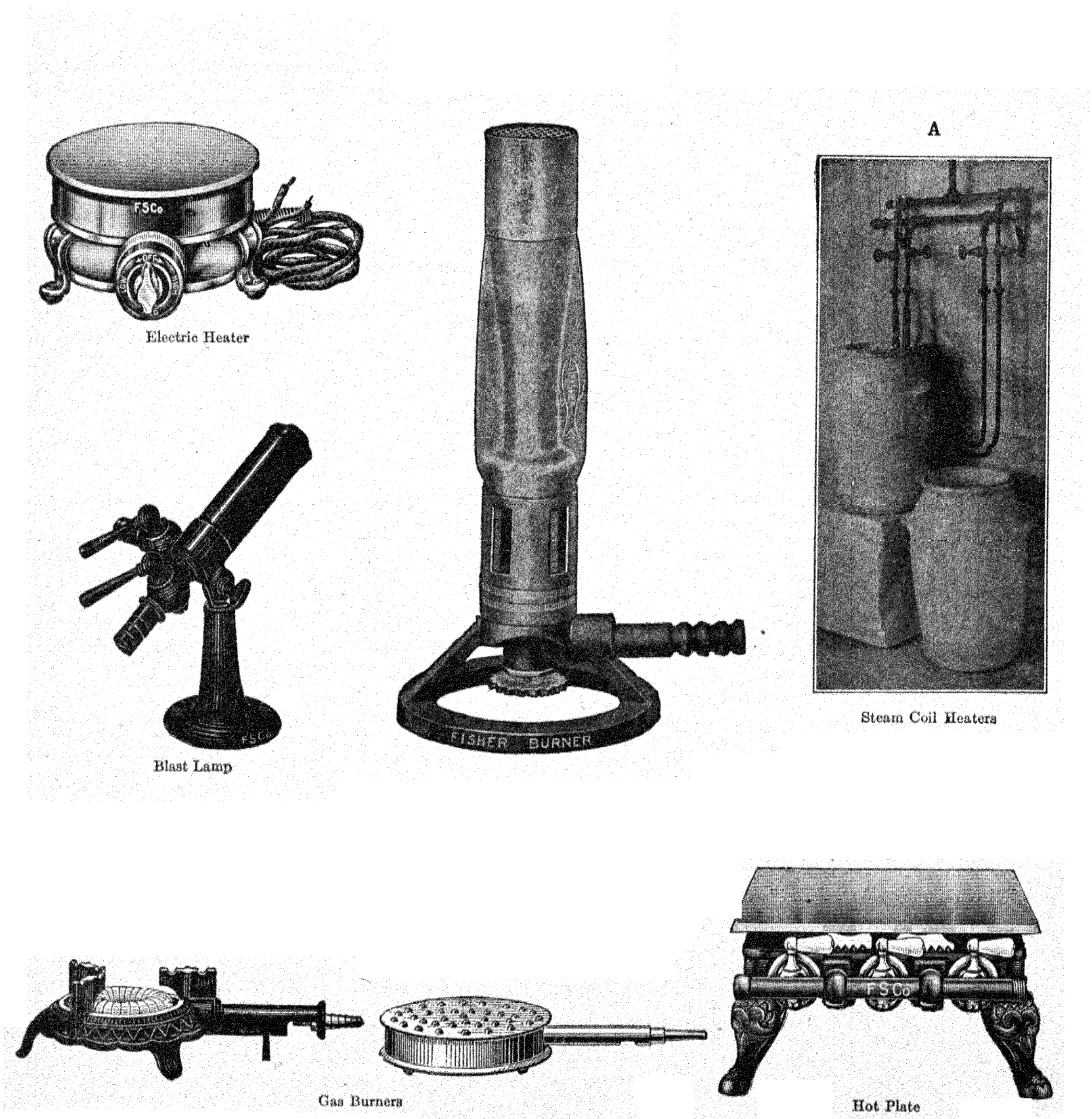
Blow over the mouth of the tube. Result:—

(*b*) **Acetyl Chloride and Alcohol.**—Place 1 cc. of absolute alcohol in a test tube. Immerse the tube in ice water and then add, drop by drop, 1 cc. of acetyl chloride. **Result:**—

Now add 1 cc. of a saturated NaCl solution. Note the odor. **Result:**—

What is the precipitate?

(*c*) **Acetyl Chloride and Ammonia.**—To. 2 cc. of ammonium hydroxide add 2 cc. of acetyl chloride, drop by drop, and shake. The acetamide formed is soluble in the water. It may be extracted with an ether-alcohol mixture (2 : 1).


Electric Heater

Blast Lamp

Steam Coil Heaters

Gas Burners

Hot Plate

FIG. 51.—Heating Devices

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EXPT. 23. ACETYL CHLORIDE

1. Write the equation for this method of preparation of acetyl chloride.

2. Why is the temperature kept below 50° at the beginning?

3. What is the function of the NaOH solution at the end of the receiver?

4. Why must acetyl chloride be kept in a well-stoppered glass container?

5. Why is it dangerous to inhale vapors from acetyl chloride?

6. Write the equation for the reaction in Expt. (*a*).

7. Write the equation for the reaction in Expt. (*b*).

8. What is the function of the NaCl solution in Expt. (*b*)?

9. Write the equation for the reaction in Expt. (*c*).

10. What other compounds may be used for the preparation of acetyl chloride?

Write the equations.

11. For what purposes is acetyl chloride used in organic chemistry?

12. What inorganic reagent is used on a commercial scale for the preparation of acyl halides?

13. Account for the precipitate formed in Expt. (*b*).

14. What are the advantages of an electric hot plate as a source of heat?

15. Why is steam extensively used as a source of heat in the organic chemical industries?

16. What substances are used in heating baths up to (*a*) 100°, (*b*) 200° and (*c*) 300° or over?

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PREPARATION OF AN ACID ANHYDRIDE

EXPT. 24. ACETIC ANHYDRIDE

Preparation.

Introduce 35 g. of finely pulverized, fused sodium acetate into a dry distilling flask, the side-arm of which is stoppered. Attach a reflux condenser. Arrange the apparatus as shown in Fig. 52. Pour 25 cc. of acetyl chloride into a dropping funnel. Set the funnel in the condenser and allow the acetyl chloride to drop gradually on to the sodium acetate. When about half of the liquid has been added, disconnect the condenser and stir the mixture with a glass rod. Connect the reflux condenser again and gradually add the remainder of the acetyl chloride. Then replace the dropping funnel with a $CaCl_2$ tube. Now place a water bath under the flask and reflux for one-half hour. At the end of this time disconnect the apparatus and rearrange according to Fig. 50, but replace the dropping funnel with a cork, omit the NaOH solution with the safety bottle and the water bath. Now heat directly with a luminous flame which is kept in constant motion until no more liquid distills over. Transfer the distillate to a dry 50 cc. distilling flask and distill, using the same type of receiver as above and having a thermometer in the distilling flask. Collect the fraction distilling over between 135°–140°. The boiling point of acetic anhydride is 137°.

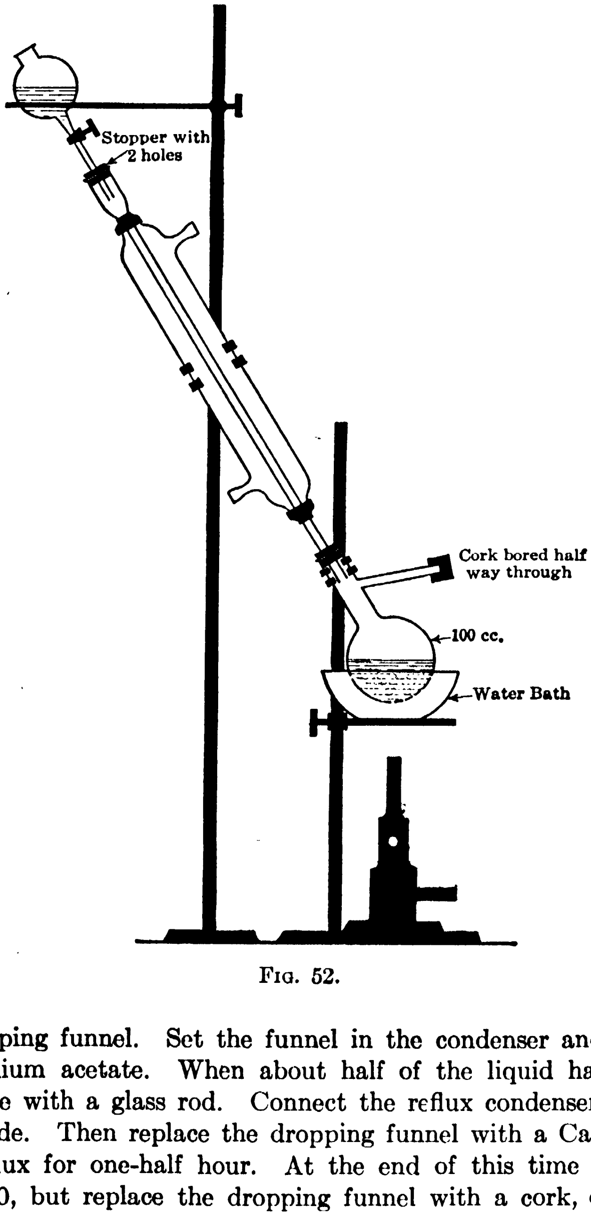

Fig. 52.

Yield = g. Calculated from the acetyl chloride = g. Percentage yield =

Properties.

(*a*) **Odor.**—Note the odor of acetic anhydride by wafting some of the vapor toward the nose.

(*b*) **Action of Water on Acetic Anhydride.**—To 5 cc. of water add 3 drops of acetic anhydride and shake. **Result:**—

Now heat. **Result:**—

Test for the compound which is formed. **Result:**—

(*c*) **Acetic Anhydride and Alcohol.**—To 2 cc. of absolute alcohol add 1 cc. of acetic anhydride and heat gently in a water bath for a few minutes. Note the odor. **Result:**—

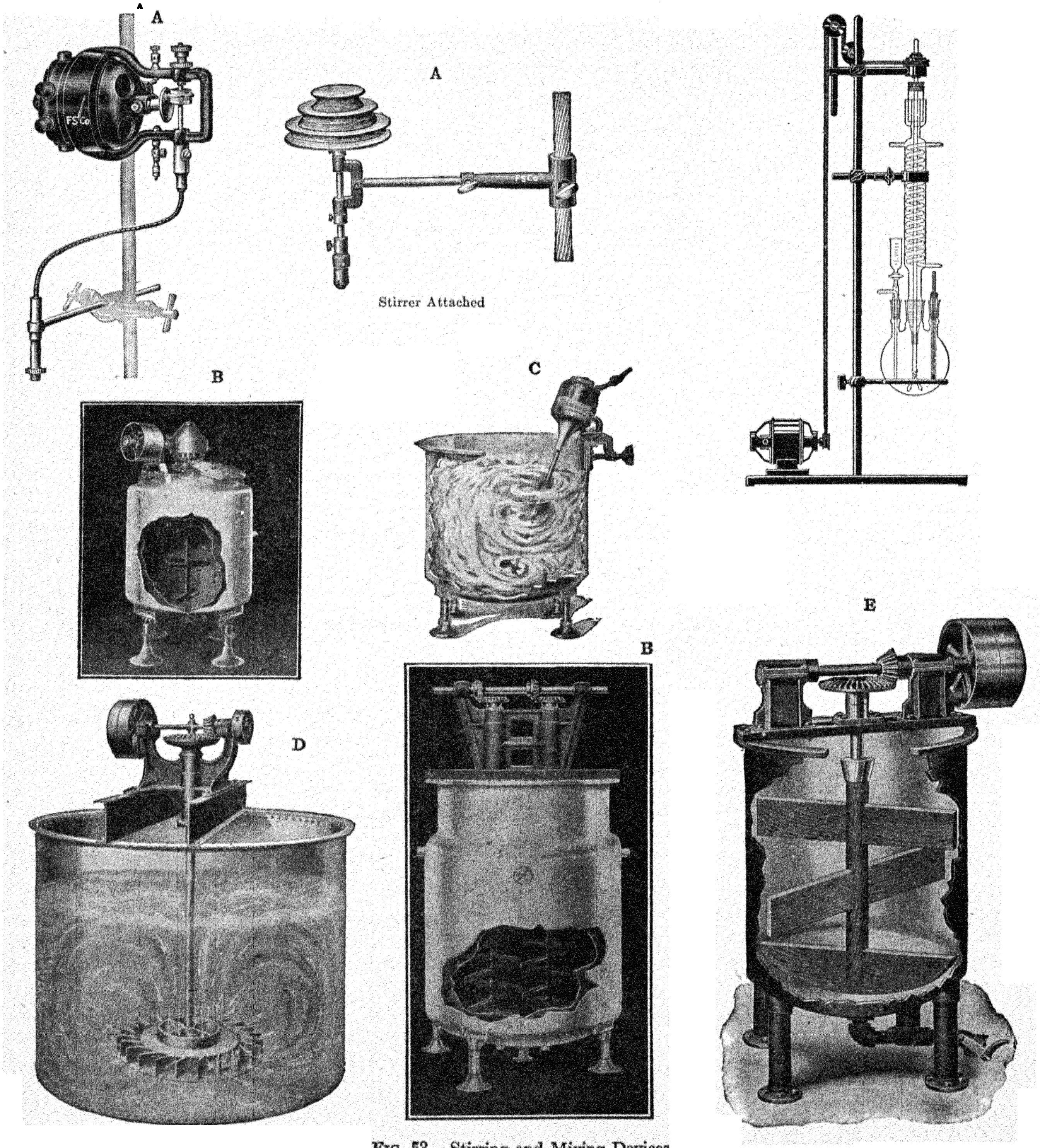

FIG. 53.—Stirring and Mixing Devices

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EXPT. 24. ACETIC ANHYDRIDE

1. Write the equation for this method of preparation of acetic anhydride.

2. Why is it necessary to stir the mixture after one-half of the acetyl chloride has been added?

3. Why is it necessary to reflux the reaction mixture?

4. Why do you use a luminous flame in this distillation?

5. Why is the apparatus in Fig. 52 set up in an oblique position?

6. Write the equation for the reaction in Expt. (*b*).

7. Write the equation for the reaction in Expt. (*c*).

8. State the uses for acetic anhydride in organic chemistry.

9. Why do you not use glacial acetic acid directly to prepare acetic anhydride?

10. What reagent would you use to prepare acetic anhydride from glacial acetic acid?

11. Why is stirring and shaking so important in conducting organic chemical reactions?

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PREPARATION OF AN ACID AMIDE

EXPT. 25. ACETAMIDE

Preparation.

Into a 500 cc. distilling flask pour 175 cc. of ethyl acetate. Add 270 cc. of ammonium hydroxide, and shake. Stopper both the side-arm and neck of the flask and set aside until the next laboratory period. Then arrange the apparatus for distillation. To the end of the condenser attach a suction flask whose side-arm is connected to a tube which reaches just to the surface of about 500 cc. of water. Heat the flask on a wire gauze. If bumping occurs put in ebullition tubes or glass beads or preferably a few pieces of porous material (from a porous plate). Test the first 5 cc. of the distillate for alcohol.

Result:—

When the temperature reaches 150°, replace the water condenser with an air condenser (only the inner tube of the water condenser), continue the heating* and collect in a beaker all the distillate that passes over between 175°–225°. Some acetamide may crystallize in the condenser. This can be removed by warming the condenser with a flame. Allow the contents of the beaker to cool. Pour off any liquid from the distillate and dry the crystals on a porous plate or between filter papers. Acetamide melts at 82°.

The acetamide obtained above is slightly impure. It may be purified by redistillation or recrystallization from chloroform or an ether-alcohol mixture (2 : 1).

Preserve the acetamide in a stoppered bottle for experiments 28 and 30.

Yield = g. Calculated = g. Percentage yield =

Properties.

(*a*) **Solubility in Water.**—To 5 cc. of water add about 0.2 g. of acetamide and shake. **Result:—**

(*b*) **Hygroscopic Nature.**—Place a few crystals of acetamide on a watch glass and allow to stand until the next laboratory period. **Result:—**

(*c*) **Odor.**—Note the odor of acetamide.

This odor is due to an impurity. Pure acetamide is practically odorless.

(*d*) **Hydrolysis with Alkali.**—Heat 1 g. of acetamide with 5 cc. of a 10 per cent solution of NaOH. Note the odor of the vapors given off. Test with red litmus paper. **Result:—**

(*e*) **Hydrolysis with Acid.**—Heat strongly 1 g. of acetamide with 10 cc. of a 10 per cent solution of H_2SO_4. The vapors of what compound are given off?

What happens to the ammonia in this reaction?

(*f*) **Action of Nitrous Acid on Acetamide.**—Dissolve 0.5 g. of acetamide in 5 cc. of water. To this solution add 0.5 g. of sodium nitrite. Cool in an ice bath. Add slowly 5 cc. of a cooled 10 per cent solution of H_2SO_4 and shake. Note the evolution of gas. What is this gas?

Carefully neutralize the solution with 5 per cent NaOH and test as in Expt. (*g*) (p. 79).

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* If uncondensed vapors appear at the end of the condenser cover its lower portion with a *damp* towel.—Use a long air condenser, if available.

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EXPT. 26. UREA

Properties.

(*a*) **Urea Nitrate.**—Dissolve 0.5 g. of urea in 2 cc. of water. Transfer to a watch glass and add 1 cc. of conc. nitric acid. Allow to stand for a few minutes. **Result:**—

(*b*) **Enzymic Decomposition.**—Dissolve 1 g. of urea in 10 cc. of water. Add 1 cc. of urease solution or 0.5 g. of powdered soya bean and allow to stand for 15–20 minutes. Now boil the liquid and test the vapors with moist red and blue litmus papers. **Results:**—

Note the odor of the evolved gas. What is it? **Result:**—

(*c*) **Action of Nitrous Acid on Urea.**—Dissolve in a test tube 0.5 g. of urea in 10 cc. of water. Add 0.5 g. of sodium nitrite. Cool in an ice mixture, and add 5 cc. of a cooled 10 per cent H_2SO_4 solution. What gases are evolved?

(*d*) **Urea and Sodium Hypobromite.**—To 5 cc. of a 10 per cent NaOH solution add 5 drops of bromine. Into this solution introduce 5 cc. of a 10 per cent solution of urea. **Result:**—

(*e*) **Biuret Formation.**—Fuse carefully in a dry test tube 1 g. of urea until a white opaque mass results. Test evolved gas with moistened litmus paper. Note the odor. **Results:**—

Allow the tube to cool. Add 5 cc. of a 10 per cent solution of NaOH. Shake vigorously and then add a few drops of a 2 per cent solution of $CuSO_4$. **Result:**—

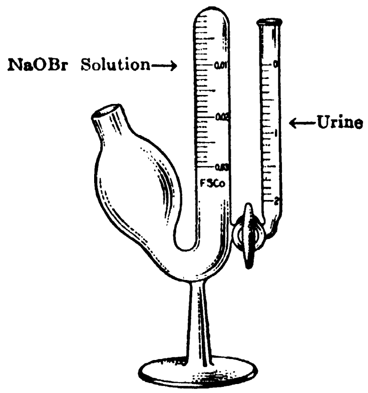

FIG. 54.—Ureometer.

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EXPT. 25. ACETAMIDE

1. Write the equation for this method of preparation of acetamide.

2. Why is a water seal attached to the receiver?

3. Why is the water condenser changed to an air condenser at 150°?

4. Write the equations for the reactions in Expt. (*d*).

5. Write the equations for the reactions in Expt. (*e*).

6. Write the equations for the reactions in Expt. (*f*).

7. Why do you add $NaNO_2$ and H_2SO_4 in Expt. (*f*) instead of HNO_2?

8. What compound would be produced if acetamide were dehydrated with P_2O_5?

9. What two graphic formulas are ascribed to acetamide?

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EXPT. 26. UREA

1. Write the equation for the preparation of urea nitrate.

2. Write the equations to show the enzymic decomposition of urea in Expt. (*b*)

3. Write the equations for the reactions in Expt. (*c*).

4. Write the equations for the reactions in Expt. (*d*).

5. Write the equation for the preparation of biuret in Expt. (*e*).

6. What is the chemical name of urea?
7. What class of foodstuffs is converted to urea in the body?
8. By which laboratory method can you determine the percentage of urea in urine?

   Outline the method.

9. Write the graphic formulas for urea and ammonium cyanate.

10. Show by graphic formulas the relationship of carbonic acid to carbamic acid and to urea.

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EXPT. 27. HYDROXY ACIDS

(*a*) **Lactic Acid.**—Pour about 30 cc. of fresh milk into a bottle. Test with blue litmus paper. **Result:—**

Stopper the bottle and set it aside until the next laboratory period. Test again with blue litmus paper. **Result:—**

The acidity of sour milk is due mainly to lactic acid.

(*b*) **Acid Nature of Fruit Juices.**—Take a piece of apple. Press to it a piece of blue litmus paper. **Result:—**

Repeat, using a slice of orange and grape. **Results:—**

(*c*) **Presence of Acids in Lemons (mainly citric acid).**—Bisect a lemon. Press out the juice into a beaker and heat to boiling. Filter and evaporate the filtrate on a wire gauze until the solution reaches one-third of its original volume. Then transfer to a water bath and evaporate to a thick syrup. Note the taste of the residue. Take a bit of the residue, dissolve it in water, and test it with blue litmus paper. **Result:—**

This residue contains citric acid.

(*d*) **Method to Prevent the Precipitation of the Hydroxides of Certain Heavy Metals.**—To 5 cc. of a 10 per cent $CuSO_4$ solution add 5 cc. of 10 per cent NaOH solution. **Result:—**

To 5 cc. of a 10 per cent $CuSO_4$ solution add 5 cc. of a 10 per cent tartaric acid solution and make alkaline with 10 per cent NaOH solution. **Result:—**

(*e*) **Reducing Action of Hydroxy Acids.**—To 2 cc. of a 10 per cent $AgNO_3$ solution add 10 per cent ammonium hydroxide solution, drop by drop, until the precipitate just dissolves, then 5 drops of a 10 per cent tartaric acid solution. Place the test tube in a hot water bath. **Result:—**

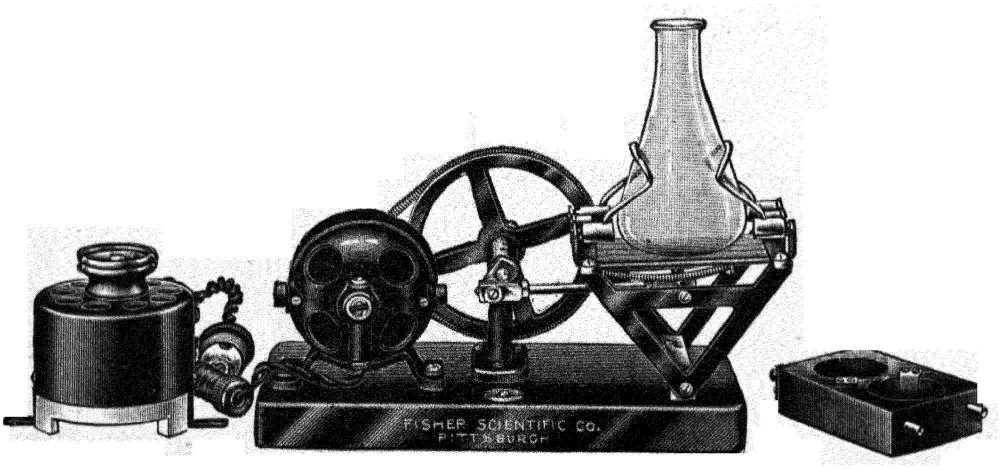

Fig. 55.—Shaking Apparatus.

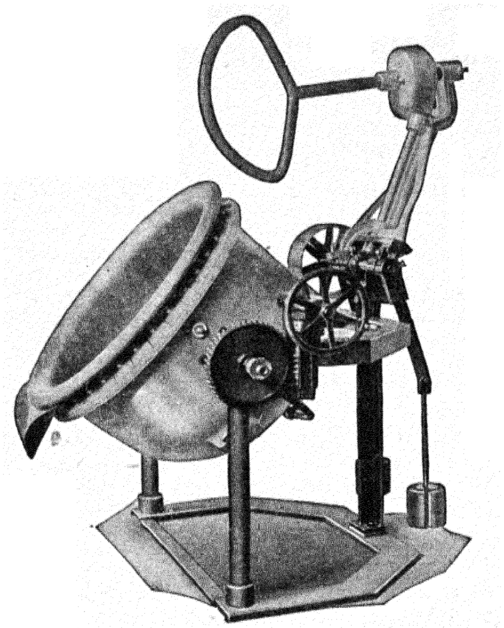

Fig. 56.—Tilting Kettle.

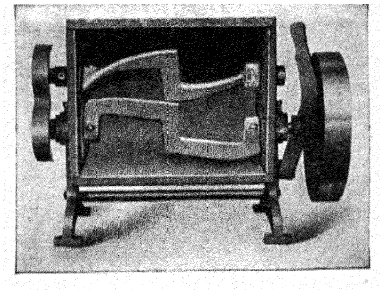

Fig. 57.—Mixer.

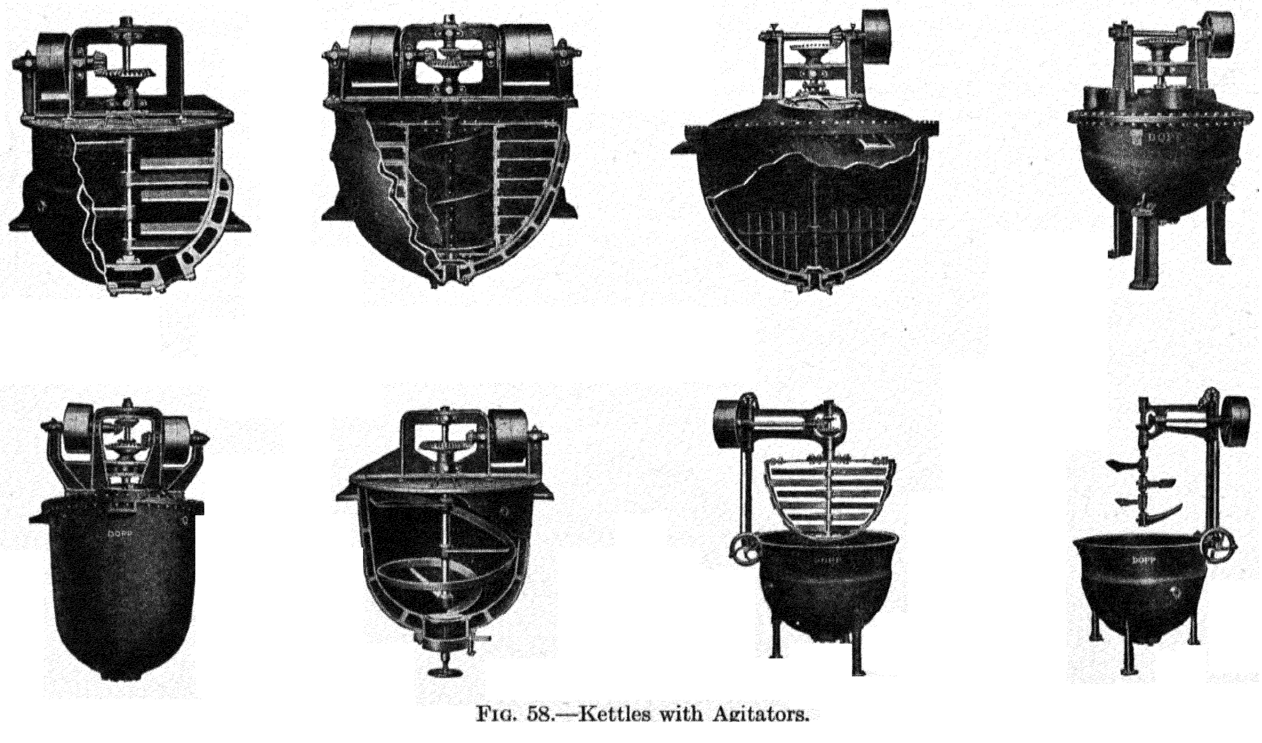

Fig. 58.—Kettles with Agitators.

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EXPT. 27. HYDROXY ACIDS

1. From what compound in milk is lactic acid produced?

2. What produces the lactic acid in milk?

3. Name several organic acids that are present in fruit juices.

4. In what industries are large quantities of citric acid and tartaric acid used?

5. Name a number of important salts of tartaric and citric acids and give their uses.

6. What branch of chemistry utilizes the principle outlined in Expt. (*d*)?

7. What grouping is present in the structure of certain hydroxy acids, i.e., tartaric acid, which renders the compound susceptible to oxidation as shown in Expt. (*e*)?

8. Discuss the occurrence of hydroxy acids in nature.

9. Summarize the general chemical properties of hydroxy acids.

10. Write the stereochemical formulas for all the tartaric acids and give their names.

Which are active and which are inactive forms?

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PREPARATION OF AN AMINE FROM AN ACID AMIDE

EXPT. 28. METHYLAMINE

Preparation.

Introduce 200 cc. of water into a 500 cc. distilling flask and add 20 g. of H T H. (See p. 45.) To this add a solution of 20 g. of sodium hydroxide in 50 cc. of water and shake. A precipitate of calcium hydroxide forms. Dissolve 12 g. of acetamide in 25 cc. of water. Slowly add this solution to the contents of the distilling flask and shake. Equip the distilling flask with a condenser and a stopper carrying a thermometer projecting into the solution so that the bulb of the thermometer is completely immersed. Use rubber stoppers. Introduce 25 cc. of distilled water into a 50 cc. beaker. By means of a stopper fit the condenser with an adapter which reaches just below the surface of the water in this beaker. Warm the flask in a water bath maintained at a temperature of 65° to 70° for half an hour; shake occasionally. The reaction is exothermic and the temperature inside the flask rises above the temperature of the water bath itself; at this time the water bath acts as a cooling bath. At the end of half an hour replace the water bath with a wire gauze and distill the methylamine by gently boiling the contents of the distilling flask. After 15 minutes replace the beaker containing the water with a 100 cc. beaker containing 50 cc. of 1 : 1 hydrochloric acid. Continue the distillation for 15 minutes longer. Concentrate the solution in the second beaker (the beaker which contained the 1 : 1 HCl solution) to one-third of its volume on a wire gauze and finally evaporate to dryness on a water bath. Grind the residue to a fine powder and agitate with 50 cc. of absolute alcohol. This dissolves the methylamine hydrochloride. Filter. The ammonium chloride remains behind. Evaporate the absolute alcohol and dry the methylamine hydrochloride.

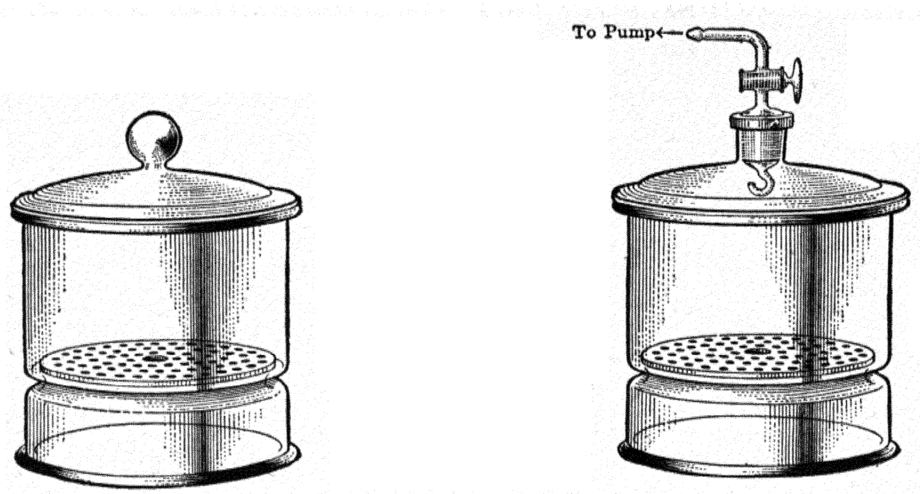
Properties.

(*a*) **Odor and Basicity.**—Dissolve about 0.5 g. of methylamine hydrochloride in water and render alkaline with 10 per cent NaOH solution. Heat gently. Note the odor by wafting some of the fumes toward the nose. Hold a piece of moistened red litmus paper in the vapors given off. **Result:**—

(*b*) **Basic Property of Amines.**—To 10 cc. of the aqueous solution of methylamine add a few drops of 10 per cent ferric chloride solution. **Result:**—

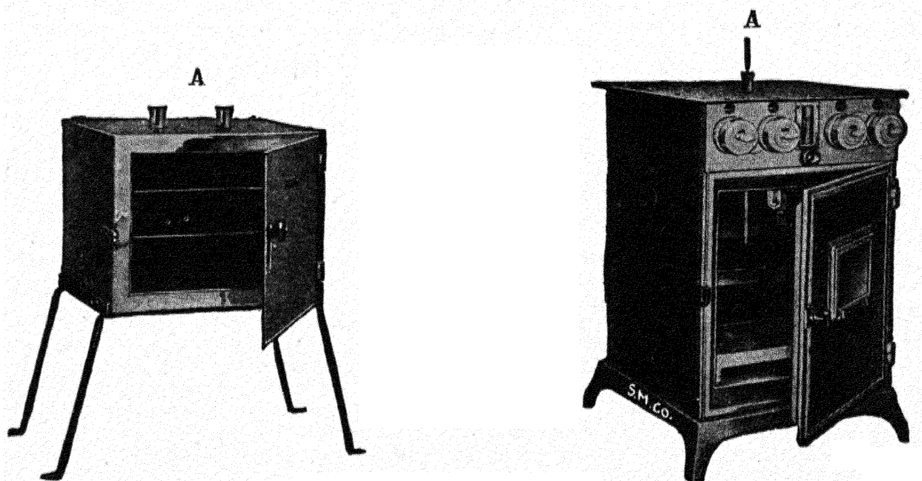
(*c*) **Reaction with $CuSO_4$.**—Add the aqueous solution of methylamine, drop by drop, to 1 cc. of a 2 per cent solution of $CuSO_4$ until a precipitate forms which redissolves in an excess of the methylamine solution.

• (*d*) **Carbylamine Test for Primary Amines.**—(Perform in hood.) Put 1 g. of methylamine hydrochloride into a test tube. Add 5 drops of chloroform and 5 cc. of an alcoholic NaOH solution (20 per cent). Warm and very carefully note the odor by wafting the vapors toward the nose. (The nauseating odor should be immediately destroyed by the addition of strong HCl. Do not pour the products into the sink before this is done.)



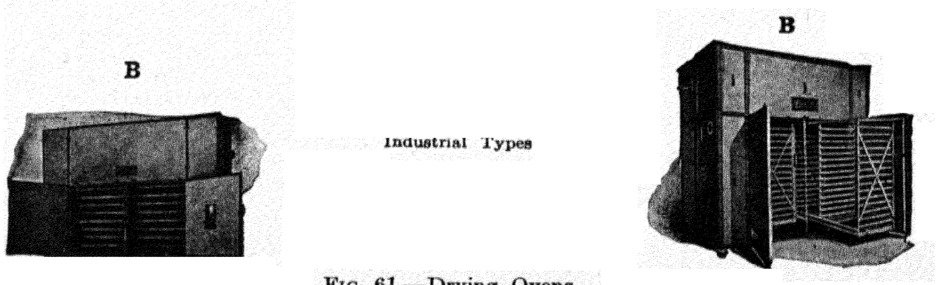
Vacuum Desiccator

Fig. 60.—Desiccators.



(Gas Heated)

(Electrically Heated)



Industrial Types

Fig. 61.—Drying Ovens.

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EXPT. 28. METHYLAMINE

1. Write the equations, step by step, for all the reactions taking place in the preparation of methylamine hydrochloride, and name the intermediate compounds formed.

2. Why does the adapter extend just below the surface of the water and HCl solutions?

3. Why is methylamine collected in HCl?

   What other compounds could be used instead of HCl?

4. Account for the formation of ammonium chloride in the receiver.

5. What is the purpose of neutralizing the $CH_3NH_2 \cdot HCl$ in Expt. (*a*)?

   Write the equation involved.

6. Show the analogous reactions of NH_3 and CH_3NH_2; ammonium salts and salts of methylamine.

7. Name methylamine hydrochloride as a derivative of ammonium chloride.

8. **Write the equation for the reaction in Expt. (*d*) and name the organic compound formed.**

9. In Expt. (28) CH_3CONH_2 is converted to CH_3NH_2. How many carbon atoms are present in each?

   Therefore what is the importance of this reaction in organic chemistry?

10. Write the equations to convert
    (*a*) $CH_3OH \rightarrow C_2H_5OH$ and
    (*b*) $C_2H_5OH \rightarrow CH_3OH$.

11. What compounds are most frequently used as drying agents in desiccators?

12. When are (*a*) desiccators and (*b*) drying ovens used?

13. What is the advantage of the vacuum desiccator over the other type shown in Fig. 60?

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EXPT. 29. PROTEINS

Properties.

(*a*) **Detection of Nitrogen.**—Mix 0.2 g. of dried egg albumin with 1 g. of soda-lime, and heat. Note the odor, and also test the vapors given off with moistened red litmus paper. **Results:**—

(*b*) **Burning Test for Proteins.**—Place a piece of egg albumin on a crucible cover, and heat gently. Note the odor. **Result:**—

PREPARATION OF A SOLUTION OF EGG ALBUMIN.—Carefully separate the white of an egg from the yolk. Put the white of the egg into a beaker and stir into it four times its volume of water. Filter through cheese-cloth. Use the filtrate for the tests indicated below.

(*c*) **Coagulation of Albumin.**—With alcohol: To 5 cc. of the egg albumin solution add 10 cc. of alcohol. **Result:**—

By heat: Heat 5 cc. of the egg albumin solution. **Result:**—

Try to dissolve the coagulated product in water. **Result:**—

(*d*) **Precipitation of Albumin.**—1. Precipitation by solutions of salts of the heavy metals: Introduce 5 cc. of the egg albumin solution into each of four test tubes. To one test tube add 1 cc. of 10 per cent $HgCl_2$; to the second tube add 1 cc. of 10 per cent $AgNO_3$; to the third tube add 1 cc. of 10 per cent $Pb(C_2H_3O_2)_2$; and to the fourth tube 1 cc. of 10 per cent $CuSO_4$. **Results:**—

2. Precipitation with strong mineral acids: Put 5 cc. of conc. HNO_3 in a test tube, incline the tube and add slowly by means of a pipette 2 cc. of the egg albumin solution. **Result:**—

This is known as Heller's test. Repeat this test, using 5 cc. of your urine in place of the egg albumin. **Result:**—

(If you obtain a positive test, report it to the instructor.)

3. Precipitation with alkaloidal reagents: Into each of five test tubes introduce 2 cc. of the egg albumin solution. To one test tube add tannic acid solution (1 per cent), drop by drop, until an excess has been added. **Result:**—

Repeat the experiment with 1 per cent solutions of picric acid, phosphomolybdic acid, phosphotungstic acid and potassium mercuric iodide. (With the last reagent use 1 drop of dilute HCl.) **Results:**—

Note if any of the precipitates are soluble in an excess of the reagent. **Results:**—

(*e*) **Color Reactions.**—1. Xanthoproteic reaction: To 3 cc. of the egg albumin solution add 3 drops of conc. HNO_3 and heat to boiling. **Result:**—

Cool and make slightly alkaline with ammonium hydroxide or sodium hydroxide solution. **Result:**—

This test indicates the presence of the phenyl grouping in the protein, therefore the presence of tryptophan, tyrosine, and phenyl alanine.

2. Biuret reaction: To 3 cc. of the egg albumin solution add 3 cc. of 40 per cent NaOH solution. Shake and add 3 drops of a 1 per cent copper sulfate solution. **Result:—**

This test is given by substances having two amino groups in the molecule.

3. Millon's reaction: To 3 cc. of the egg albumin solution add 5 drops of Millon's reagent. **Result:—**

Heat to boiling. **Result:—**

This test indicates the presence of the hydroxyphenyl group in the protein, therefore the presence of tyrosine, etc.

4. Glyoxylic acid (Hopkins-Cole) reaction: To 3 cc. of the egg albumin solution add 2 cc. of glyoxylic acid solution and shake. Incline the tube and carefully pour down the side 5 cc. of conc. H_2SO_4. Allow to stand for 5 minutes. **Result:—**

This test indicates the presence of tryptophan.

(*f*) **Test for Proteins in Various Substances.**—Test for protein in the following substances: bread, gelatin, milk, nuts, butter, flour and wool. **Results:—**

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EXPT. 30. ACETONITRILE

Preparation.

Place 15 g. of dry acetamide and 25 g. of phosphorus pentoxide in a 200 cc. distilling flask. Shake the mixture. Then set up a distilling apparatus with a condenser and a small flask as a receiver. Heat the flask directly with a large luminous flame kept in constant motion. Collect the distillate up to 150°. To purify the distillate, treat it with half its volume of water in a small separatory funnel, shake and add solid potassium carbonate until no more dissolves. Allow to stand. Separate the upper layer. Transfer it to a dry 50 cc. distilling flask, add 3 g. of phosphorus pentoxide and distill. Collect the fraction between 81°–83°. Pure acetonitrile boils at 82°.

Yield = g. Calculated = Percentage yield =

Properties.

(*a*) **Odor.**—Note the odor of acetonitrile. **Result:—**

(*b*) **Reduction of a Nitrile.**—Dissolve 1 cc. of acetonitrile in 10 cc. of alcohol. Place the test tube in an ice bath and add a small piece of metallic sodium (size of a pea). After a few minutes test the solution for a primary amine according to Expt. (*d*) (p. 112). **Result:—**

(*c*) **Alkaline Hydrolysis of a Nitrile.**—To 1 cc. of acetonitrile add 10 cc. of a 20 per cent NaOH solution and warm until no more ammonia is given off. Neutralize with 10 per cent HCl and test the solution for acetic acid according to Expt. (*g*) (p. 79). **Result:—**

(*d*) **Acid Hydrolysis of a Nitrile.**—Put 5 cc. of acetonitrile in a 50 cc. distilling flask, add 20 cc. of 25 per cent H_2SO_4 solution and reflux on a water bath for $\frac{1}{2}$ hour. Then distill off 10 cc. of the liquid and test for acetic acid according to Expt. (*g*) (p. 79). **Result:—**

Render the residue in the flask alkaline, heat and test for the evolved ammonia. **Result:—**

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EXPT. 29. PROTEINS

1. Why is the white of the egg diluted with water in preparing the solution of egg albumin?

2. What conclusion do you draw from the result of Expt. (c)?

3. Is the coagulation of albumin a physical or a chemical change?

Give experimental evidence for your answer.

4. Name the salts of the heavy metals whose solutions precipitate proteins as in Expt. (*d*).

5. What does the presence of albumin in urine indicate?

6. Account for the yellow stain sometimes appearing on your hands when working in the laboratory.

7. Do foods containing protein undergo chemical change during the process of drying or baking?

Give the experimental evidence for your answer.

8. Give the name of the test reagents used and the colors produced in each of the experiments under (*e*).

9. As what compound is most of the ingested protein eliminated from the body?

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EXPT. 30. ACETONITRILE

1. Write the equation for the reaction used in the preparation of acetonitrile.

2. What is the function of the P_2O_5?

3. What is the function of the K_2CO_3?

4. Why is the additional amount of P_2O_5 added in the final distillation?

5. Compare the odor of a cyanide with that of an isocyanide.

6. Write the equations for the reactions in Expt. (*b*).

7. Why is the test tube in Expt. (*b*) inserted in an ice bath?

8. Write the equations for the reactions in Expt. (*c*).

9. Write the equations for the reactions in Expt. (*d*).

10. $CH_3X + NaCN \rightarrow CH_3CN \rightarrow CH_3COOH$. What is the importance of such a series of reactions in organic chemistry?

11. Write the equations for all the reactions involved in the conversion of ethyl bromide to propionic acid.

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EXPT. 31. CARBOHYDRATES AND RELATED COMPOUNDS

GLUCOSE

NOTE.—Make up 50 cc. of a 10 per cent solution of glucose. This is to be used in the experiments given below wherever glucose solution is called for. If all the experiments are not completed the same day, make up a fresh solution.

(*a*) **Molisch Test.**—To 3 cc. of the glucose solution add 2 drops of Molisch's reagent (10 per cent solution of α-naphthol in chloroform). Introduce 5 cc. of conc. H_2SO_4 into a test tube. Hold the tube in an inclined position and slowly add the mixture prepared above. **Result:**—

This test is given by all substances containing carbohydrates.

(*b*) **Glucose and Alkalies.**—Repeat Expt. (*i*) (p. 63). Result:—

(*c*) **Test with Schiff's Reagent.**—To 5 cc. of the glucose solution add 1 cc. of Schiff's reagent. **Result:**—

(*d*) **Reducing Property of Glucose.**—1. Silver mirror test: Test 1 cc. of the glucose solution as in Expt. (*g*) (p. 63). **Result:**—

2. Fehling's Solution: Test 1 cc. of the glucose solution as in Expt. (*c*) (p. 68). **Result:**—

Repeat this test, using 5 cc. of your urine in place of the glucose. **Result:**—

(If you obtain a positive test, report it to the instructor.)

3. Nylander's solution (bismuth reduction): To 5 cc. of the glucose solution add 0.5 cc. of Nylander's reagent and heat on a water bath for 5 minutes. The solution will first darken and then, after a few minutes, a black precipitate will appear (finely divided bismuth).

4. Picric acid test: To 5 cc. of the glucose solution add 0.5 g. of Na_2CO_3 and 2 cc. of a saturated solution of picric acid. Heat. **Result:**—

The picric acid is reduced to picramic acid.

$$HO \cdot C_6H_2 \cdot (NO_2)_3 \rightarrow HO \cdot C_6H_2 \cdot NH_2(NO_2)_2$$

NOTE.—The tests employed for detecting the presence of reducing sugars in physiological products are based on their reducing property. Expts. (*d*)2 and (*d*)3 being especially used in the case of urine, and Expt. (*d*)4 in that of blood.

(*e*) **Phenylglucosazone Formation.**—Thoroughly grind together in a mortar ½ g. of phenylhydrazine hydrochloride and 1 g. of hydrated sodium acetate. To this mixture in a test tube add 10 cc. of the glucose solution. Shake, and heat in a boiling water bath for ½ hour. Cool and set aside. **Result:**—

(*f*) **Fermentation.**—Refer to the preparation of alcohol Expt. 13 (p. 55).

SUCROSE

(*g*) **Solubility.**—Test the solubility of sucrose in water, alcohol, and ether. **Results:**—

(*h*) **Effect of Heat on Sucrose.**—Place 3 g. of sugar in a small porcelain dish. Heat on a sand bath until the sugar melts and becomes yellowish brown in color. Remove a portion, cool and taste. This is called "barley sugar"; it is used in candy. Heat the remainder at about 200° (thermometer in sand bath) for 10-15 minutes until the mass becomes dark brown in color. This is called "caramel" and is used as a coloring material in foodstuffs. Cool, taste, and determine its solubility in water. **Result:—**

(*i*) **Sucrose and Phenylhydrazine.**—Try the action of sucrose with phenylhydrazine as in Expt. (*e*) **Result:—**

(*j*) **Test with Fehling's Solution.**—Try the action of Fehling's solution on about 1 cc. of 10 per cent sucrose solution. **Result:—**

(*k*) **Inversion of Sucrose.**—Introduce into a small beaker a solution of 1 g. of sucrose in 25 cc. of water. Add 1 cc. of 10 per cent HCl solution. Boil for 5 minutes, cool, and neutralize with 10 per cent NaOH solution. Test the resulting liquid with Fehling's solution. **Result:—**

LACTOSE

(*l*) **Properties of Lactose.**—Test lactose with phenylhydrazine and Fehling's solution.

After heating the phenylhydrazine-lactose mixture, allow it to cool. **Result:—**

PENTOSANS

(*m*) **Hydrolysis of Gum Arabic.**—To a lump of gum arabic (the size of a pea) add 5 cc. of HCl (1 : 1) and boil for 10 minutes on a water bath. Cool, neutralize with NaOH solution and test with a solution of aniline acetate (1 part of acetic acid to 1 part of aniline shaken together). Note the immediate result and the result on standing.

DEXTRIN

(Make about 30 cc. of a 10 per cent dextrin solution.)

(*n*) **Iodine Test.**—To 5 cc. of the dextrin solution add a drop of iodine in KI solution. **Result:—**

(*o*) **Test with Fehling's Solution.**—Test 1 cc. of the dextrin solution with Fehling's solution. **Result:—**

Pure dextrin does not reduce Fehling's solution. If you obtain reduction in this experiment, to what compounds is it due?

(*p*) **Hydrolysis of Dextrin.**—To 20 cc. of the dextrin solution in a small beaker add 5 drops of conc. HCl solution. Boil, and test as in Expt. (*d*)2. **Result:—**

STARCH

(*q*) **Preparation of Potato Starch.**—Pare a potato and grate it. Mix the grated material with enough water to make a pulp. Beat up this pulp thoroughly and filter it through cheese-cloth. Set aside the filtrate for a few minutes to allow the starch particles to settle out. Pour off the supernatant liquid and wash the residue three times with water. Filter through a filter paper, allow residue to drain well and then spread it out to dry. What are the granules?

(*r*) **Iodine Test.**—1. Place about 0.1 g. of corn-starch on a small watch glass. Add 1 cc. of water and stir. Add a drop of a solution of iodine in potassium iodide. **Result:—**

2. Prepare a starch paste by grinding 1 g. of starch with 5 cc. of water in a mortar. Pour this mixture with constant stirring into 100 cc. of boiling water, and allow it to cool. To 1 cc. of the paste add 100 cc. of water. Introduce 3 cc. of this diluted starch paste into a test tube and add 1 drop of a dilute iodine in potassium iodide solution. **Result:—**

Heat to boiling. **Result:—**

Set aside to cool. **Result:—**

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EXPT. 31. CARBOHYDRATE AND RELATED COMPOUNDS (*Continued*)

(*s*) **Test with Fehling's Solution.**—Introduce 2 cc. of the undiluted starch paste into a test tube and test with Fehling's solution. **Result:**—

(*t*) **Hydrolysis of Starch with Acid.**—To 50 cc. of the undiluted starch paste in a beaker add 1 cc. of conc. HCl, and heat. At two-minute intervals remove 1 cc. of the solution and test with iodine in potassium iodide solution. When the solution ceases to give a test for starch or dextrin with the iodine solution, cool, and neutralize with dilute NaOH solution. Test with Fehling's solution. **Result:**—

(*u*) **Hydrolysis of Starch with Saliva.**—(Start at the beginning of the laboratory period.) Collect 5 cc. of saliva in a test tube. The flow of saliva may be promoted by chewing a piece of paraffin or psychologically induced by thinking of lemon, etc. Add one drop of a dilute iodine in KI solution and 2 cc. of the starch paste. Occasionally shake and allow the tube to stand until the blue color disappears. Immediately test the liquid with Fehling's solution. **Result:**—

CELLULOSE

(*v*) **Addition of Iodine Solution.**—Put a drop of iodine in KI solution on a small piece of absorbent cotton. **Result:**—

(*w*) **Parchment Paper.**—Make an H_2SO_4 solution by slowly pouring 40 cc. of conc. H_2SO_4 into 20 cc. of water. *Cool* to room temperature and place a strip of filter paper in the solution. Remove the filter paper after exactly 15 seconds, wash thoroughly in running water, and test a portion of the paper with iodine in KI. **Result:**—

Hang up the remainder of the paper to dry. Compare it in appearance and toughness with a piece of the original filter paper.

(*x*) **Hydrolysis of Cellulose.**—To a small piece of cotton add 4 or 5 drops of conc. H_2SO_4. Allow to stand for 2 minutes. Then dilute with 25 cc. of water and boil for 20–30 minutes. Filter, and neutralize with 25 per cent Na_2CO_3 solution. Test with Fehling's solution. **Result:**—

(*y*) **Cellulose Acetate.**—Into a dry small Erlenmeyer flask introduce 20 cc. of glacial acetic acid and 4 drops of H_2SO_4 ($1\frac{1}{2}\%$). Add two grams of absorbent cotton, press it into the acetic acid and allow to stand for 3 hours. Then add 10 cc. of acetic anhydride and stir the mixture thoroughly. Cover with a watch glass and allow to stand until the next laboratory period. **Result:**—

Pour the resulting solution slowly and with constant stirring into 300 cc. of water. **Result:**—

Filter by suction, wash with water and press well between filter papers. Dissolve about 0.2 g. of the pressed product in 20 cc. of chloroform. Pour the solution on to a clock glass and allow it to evaporate. Pry an edge of the film loose with a knife and pour water under the film to separate it from the glass. Dry the film in air. Test the flammability of the film. **Result:**—

Also test the solubility of the product in acetone, ether and alcohol. **Results:**—

(*z*) **Cellulose Nitrate.**—Press about 0.5 g. of absorbent cotton into a mixture of 20 cc. of conc. H_2SO_4 and 10 cc. of conc. HNO_3. Allow to stand for 2–3 minutes. Remove the nitrated cotton, wash thoroughly with cold water, press out as much liquid as possible, shred, and spread on a watch glass to dry until the next laboratory period. (Caution.) Test the flammability of the dried product. **Result:**—

Also test the solubility in alcohol, ether, and an ether-alcohol mixture (1 : 1). **Results:—**

Pour the ether-alcohol solution upon a watch glass and allow to evaporate. Remove the film as in the above experiment, dry in air and test its flammability. **Result:—**

Compare the flammability of cellulose acetate with cellulose nitrate.

(*aa*) **Solubility of Cellulose in Schweitzer's Reagent.**—To 100 cc. of a 5 per cent $CuSO_4$ solution, which contains 5 per cent ammonium chloride, add 10 per cent sodium hydroxide solution, drop by drop, and shake until precipitation is complete. (The appearance of a deep blue color indicates excess of NaOH solution.) Filter, and wash the precipitate of copper hydroxide several times with water. To 20 cc. of conc. ammonium hydroxide add as much of the cupric hydroxide as will dissolve. This is Schweitzer's reagent. Put into this solution about 0.2 g. of absorbent cotton, stopper and allow to stand until the next laboratory period. Filter and reprecipitate the cotton by acidifying with 20 per cent HCl.

(*bb*) **Viscose.**—Place 2 g. of surgical cotton in a 100 cc. wide-mouth bottle (the type used to collect gases). Add 22 cc. of a cold 20 per cent NaOH solution. Thoroughly stir the cotton in the NaOH solution for 10 minutes until uniformly wet. Allow the mixture to stand 20 minutes longer. Remove the cotton and thoroughly squeeze out the excess of NaOH solution (use rubber gloves provided for this purpose). Place the shredded, squeezed-out cotton in another 100 cc. heavy-wall, wide-mouth bottle and add 3 cc. of CS_2. Seal at once with a tightly fitting rubber stopper. Allow to stand for 2 hours. Shake occasionally to facilitate uniform reaction. At the end of this time the reaction product should have a bright orange color. Remove the stopper and remove the excess CS_2 by suction. Add 25 cc. of a 10 per cent NaOH solution. Stopper the bottle and set in the ice box until the next laboratory period.

With a heavy stirring rod mix the contents until all lumps have disappeared. Add 50 cc. of water, stir until a smooth and uniform product results. This is the viscose solution.

Syneresis.—Pour some of the viscose into a test tube and close the tube with a rubber stopper to prevent evaporation. Allow this tube to stand in the desk for at least a month, observing all the changes that occur. **Result:—**

Films.—Coat a test tube by immersing it half-way in the viscose. Support the tube, mouth upwards, and allow the viscose to drain for 15 minutes. Invert the tube and let it stand for another 15 minutes. During these periods, make up a saturated solution of ammonium sulfate and add a small amount of dilute H_2SO_4. Immerse the coated tube in this solution, being careful not to touch the viscose to the beaker as this will mar the film. When the film has become chalky white, remove the test tube and slip off the film. Place the film in 5 per cent sulfuric acid for 5 minutes. Wash it thoroughly to free it from all acid.

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EXPT. 31. CARBOHYDRATES AND RELATED COMPOUNDS

1. What characteristic group in glucose is responsible for the tests in Expts. (*b*), (*d*), and (*e*)?

2. Write the equations, step by step, for the reactions in Expt. (*e*) and name the products formed.

3. Write the graphic formula for sucrose.

Why are there no reactions with the reagents in Expts. (*i*) and (*j*)?

4. Write the equation for the reaction in Expt. (*k*) and name the compounds formed.

What is the function of the HCl in this Expt.?

5. Write the graphic formula for lactose.

Why are there reactions with the reagents in Expt. (*l*)?

6. Define (*a*) pentose and (*b*) pentosan and give examples.

7. What compound is produced in Expt. (*m*) which gives the color reaction with aniline acetate solution?

Illustrate by graphic formulas the formation of this compound from a pentose.

8. Name several different starches.

9. Tabulate in order the hydrolytic products of starch as shown in Expt. (*t*), and give the corresponding colors produced by each with the iodine solution.

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EXPT. 31. CARBOHYDRATES AND RELATED COMPOUNDS—(*Continued*)

10. What substance in saliva produces the chemical changes shown in Expt. (*u*)?

11. What are the natural sources of cellulose?

12. Write the equation for the reaction in Expt. (*x*).

13. Mention uses for cellulose acetate and cellulose nitrates.

    Why is cellulose acetate preferred in the industries?

14. What are the components of collodion?

15. What is meant by the term "sized muslin"?

16. What biological substances may be used in place of acids to

17. In what form are the ingested carbohydrates eliminated from the body?

18. Phenylhydrazine is used for the identification of sugars. Why?

19. Why is the formula $(C_6H_{10}O_5)_x$ ascribed to pure cellulose, starch, dextrin, etc.?

20. Explain the chemical reactions involved in the preparation of viscose.

Give uses for viscose.

21. How are the following substances prepared:—
(*a*) caramel; (*b*) amyloid; (*c*) mercerized cotton; (*d*) pyroxylin; (*e*) celluloid; (*f*) nitro-starch; (*g*) cordite and (*h*) rayon.

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EXPT. 32. DESTRUCTIVE DISTILLATION OF SOFT COAL

Into a 20 cm. hard-glass test tube introduce particles of soft coal (less than pea size) until the tube is filled to within about 4 cm. Arrange the apparatus as shown in Fig. 62. Add 2 cc. of H_2SO_4 to the water in the bottle. Gently tap the tube until a channel is formed above the coal. Heat the tube along its entire length, gradually raising the temperature to a red heat, and keeping the flame in constant motion. After heating for 3 minutes hold a flame at the end of the constricted tube (*A*). **Result:—**

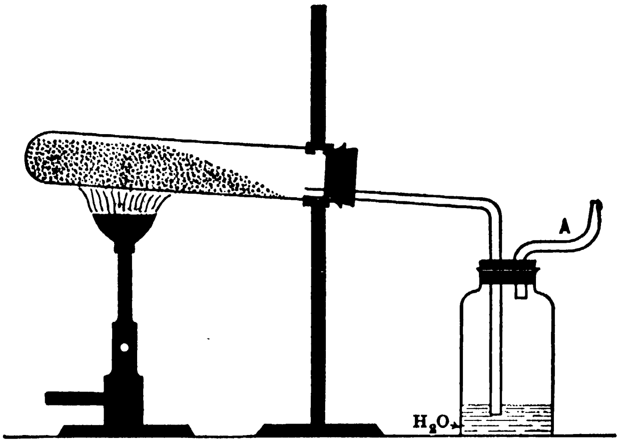

FIG. 62.

When gas no longer bubbles through the water, discontinue the heating and immediately remove the stopper from the test tube. Examine the contents of the test tube (after it has cooled) and also of the bottle. **Results:—**

Pour 10 cc. of the contents of the bottle into a test tube. Add 5 cc. of 10 per cent NaOH solution. Heat and test the evolved gas by holding a piece of moistened red litmus paper at the mouth of the tube. **Result:—**

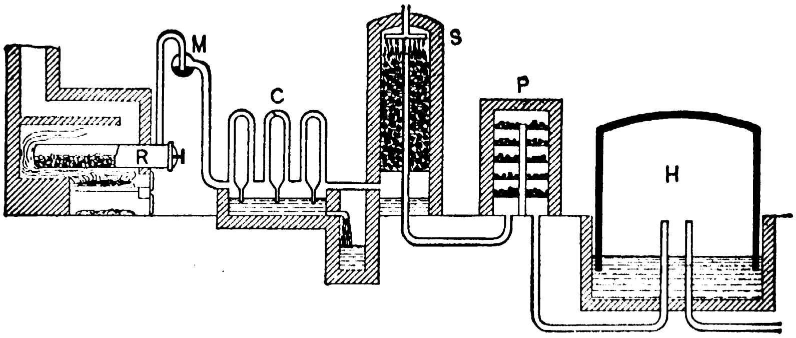

FIG. 63.—Diagram of a Plant for Making Coal Gas.

R—Retort
M—Hydraulic Main
C—Tar Condensers
S—Scrubbing Tower
P—For Removing H_2S
H—Gas Holder

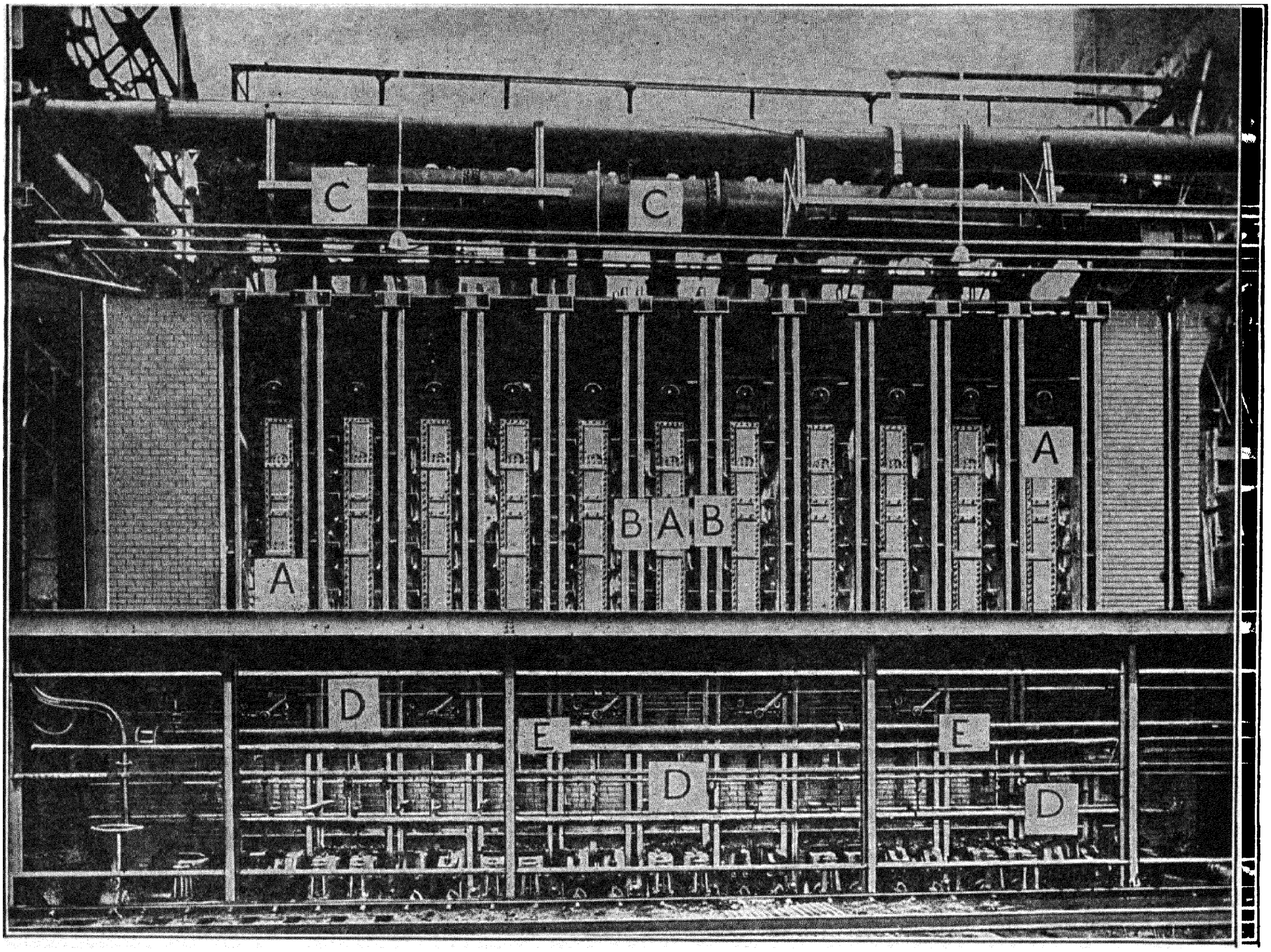

FIG. 64.—Battery of Becker Gas Ovens.

A—Oven (retort) containing coal.
B—Each oven is located between two heating walls.
C—Collecting main through which gas, tar and ammonia pass to by-product recovery plant.
D—Regenerators (brick checker work) in which heat extracted from waste flue gases is stored and later absorbed by incoming air to aid combustion.
E—Coal gas main. A part of the coal gas produced in the ovens may be returned through E and burned in the heating walls B. In place of coal gas, other fuel gases may be used.

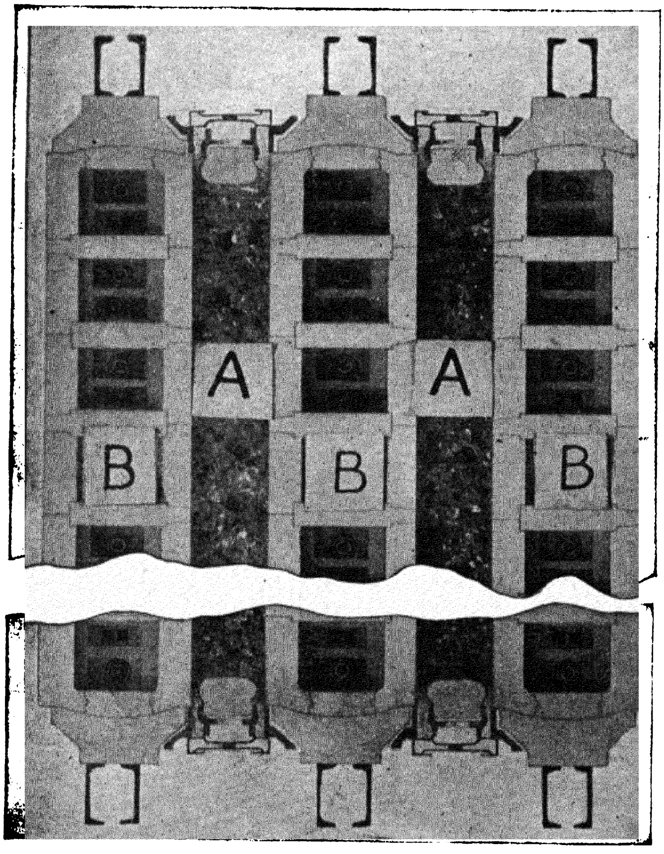

FIG. 65.

FIG. 65.—Cross-section of Becker Gas Ovens showing Coal in Two Oven Chambers, also Three Heating Walls.

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EXPT. 32. DESTRUCTIVE DISTILLATION OF SOFT COAL

1. What is the advantage of using small particles of soft coal in this experiment?

2. Why do you wait about 3 minutes before you ignite the gas at the tip (*A*)?

3. Why use bituminous coal instead of anthracite coal?

4. What are the products of the destructive distillation of coal as observed in this experiment?

5. What is the composition of coal gas?

   What main classes of hydrocarbons in the gas are responsible for the luminosity of the flame

6. Describe the physical nature of coal tar.

7. Commercially, what important organic compounds are separated from coal tar?

8. Name the uses for the ammoniacal liquor.

9. Why must H_2S be removed from coal gas before the latter is suitable for domestic use?

   What substances are used to remove the H_2S?

10. Arrange a schematic outline for the distillation of coal, showing (*a*) the primary products obtained, (*b*) the products directly obtained from the fractional distillation of coal tar and (*c*) the important commercial organic compounds recovered.

11. What is the purpose of adding H_2SO_4 to the water in the bottle in Fig. 62?

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EXPT. 33. BENZENE AND TOLUENE

Properties.

(*a*) **Odor.**—Note the odor of benzene and toluene.

(*b*) **Solubility.**—Test the solubility of benzene in water, alcohol and ether. **Results:**—

Which is heavier, benzene or water?

(*c*) **Solvent Action of Benzene.**—Test the solubility of lard, iodine, rosin, and rubber in benzene. **Results:**—

(*d*) **Test for the Presence of Thiophene in Benzene.**—Drop a crystal of isatin into 1 cc. of conc. H_2SO_4. Add 3 cc. of commercial benzene and shake. **Result:**—

Repeat, using pure benzene. **Result:**—

(*e*) **Flammability.**—(Hood). Place 1 cc. of benzene in a small evaporating dish and ignite. **Result:**—

(*f*) **Bromination of Benzene.**—To 4 cc. of benzene in a 20 cm. test tube add 1 cc. of bromine. In another tube repeat this and carefully add a few pieces of iron filings. Cool, if necessary. **Results:**—

Occasionally blow across the mouth of both tubes. **Results:**—

At the end of the laboratory period, stopper and allow to stand in your locker (in darkness) until the next laboratory period. To each tube add 25 cc. of water. Stir. **Results:**—

(*g*) **Action of Nitric Acid on Benzene.**—See Expt. 35 (p. 139).

(*h*) **Action of Fuming H_2SO_4 on Benzene.**—See Expt. 34 (p. 135).

(*i*) **Benzene and $KMnO_4$ Solution.**—Introduce 5 cc. of benzene and 1 cc. of a 0.01 per cent $KMnO_4$ solution into a test tube and shake. **Result:**—

Compare with Expt. (*d*) (p. 26); and (*c*) (p. 33).

(*j*) **Oxidation of a Side Chain.**—Place 5 cc. of toluene in a 100 cc. Erlenmeyer flask. Add 40 cc. of a *cold* 20 per cent H_2SO_4 and 3 g. of powdered $KMnO_4$. Attach a reflux condenser and heat gently for 2 hours on an asbestos pad. Loosen the condenser clamp and shake frequently. Cool and extract the mixture twice with 10 cc. of ether. Pour the ether solution on a watch glass and allow to stand in the hood until all the ether has evaporated. What is the compound produced?

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EXPT. 33. BENZENE AND TOLUENE

1. Why is thiophene always present in commercial benzene?

2. Why keep all flames away from benzene?

3. Write the equation for the reaction in Expt. (*f*) and name the organic compound produced.

4. Explain the function and theory of the halogen carrier.

5. Write the equation for the reaction in Expt. (*g*) and name the compound formed.

6. Write the equation for the reaction in Expt. (*h*) and name the compound formed.

7. Compare the chemical properties of the aliphatic hydrocarbons with those properties studied for benzene.

8. Write the equation for the reaction in Expt. (*j*) and name the organic compound produced.

9. What product would result if the side chain of ethyl benzene were oxidized?

10. What oxidizing agents besides $KMnO_4$ may be used?

11. What is meant by the terms (*a*) benzine, (*b*) benzol and (*c*) benzene?

12. Give the chief source of benzene and toluene.

13. Give uses for benzene and toluene.

14. Discuss the chlorination of toluene under various conditions and name the compounds produced

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SULFONATION OF AN AROMATIC HYDROCARBON

EXPT. 34. SODIUM BENZENESULFONATE

Preparation.

Carefully pour 112 g. of fuming sulfuric acid (sp. gr. 1.87) into a 300 cc. flask. Attach a reflux condenser. In portions of 5 cc. add 37 cc. of benzene. Shake after each addition and wait until each portion has dissolved or reacted before adding another (no benzene layer on surface of the fuming H_2SO_4). During this operation the temperature should be kept below 60°, cooling if necessary. After all the benzene has been added shake 10 minutes longer. Remove the condenser, add the reaction mixture, drop by drop, with constant stirring into 400 cc. of a filtered saturated solution of NaCl.* Cool in an ice bath for 2 hours. If the separation of crystals is slow this may be hastened by scratching the side of the beaker with a stirring rod. When the sodium benzenesulfonate has separated, filter by suction, wash the residue with a small amount of saturated NaCl solution. Transfer the residue to a porous plate, spread out in as thin a layer as possible, and allow to dry until the next laboratory period. The crystals may be further dried by heating in an oven at 110°.

Yield = g. Theoretical = g. Percentage yield =

Properties.

(*a*) **Salts of Benzenesulfonic Acid.**—Dissolve 1 g. of sodium benzenesulfonate in 10 cc. of water. To this solution add 10 cc. of a 10 per cent lead acetate solution. Warm gently and cool in ice water. **Result:**—

Repeat using a 10 per cent zinc chloride solution instead of the lead acetate solution. **Result:**—

(*b*) **Separation of the Sulfonic Acid from Sulfuric Acid.**—Add about 3 g. of sodium benzenesulfonate to about 5 cc. of H_2SO_4 (1 : 5) solution. Slowly add a suspension of $BaCO_3$ until gas is no longer evolved. Boil and filter. The residue is $BaSO_4$ and excess of $BaCO_3$. The filtrate contains barium benzenesulfonate. To the filtrate add a few cubic centimeters of conc. Na_2CO_3 solution. The precipitate is $BaCO_3$. Filter. The filtrate contains sodium benzenesulfonate.

BENZENESULFONYL CHLORIDE

To 25 g. of dry sodium benzenesulfonate in a dry 150 cc. flask add gradually (under the hood) 30 g. of finely divided phosphorus pentachloride. Mix by thorough shaking for a few minutes. Heat the mixture on a water-bath for ½ hour. Allow to cool and transfer the reaction product to a beaker containing 250 cc. of ice water. Wash out the contents of the flask with ice water and add it to the mixture in the beaker. Stir the ice water mixture frequently during a period of 2 hours. Then extract the benzenesulfonyl chloride with ether. Repeat the extraction. Filter the ethereal solution and distill off the ether. **Result:**—

BENZENESULFONAMIDE

To 2 cc. of the benzenesulfonyl chloride add ammonium hydroxide, 1 cc. at a time, and with constant shaking, until the odor of the benzenesulfonyl chloride has disappeared, and a solid has formed. Filter, and wash twice with cold water. **Result:**—

Preserve the remainder of the sodium benzenesulfonate for the preparation of phenol (p. 151).

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* For explanation of "Salting Out" see Gattermann's "Practical Methods of Organic Chemistry" (General Part).

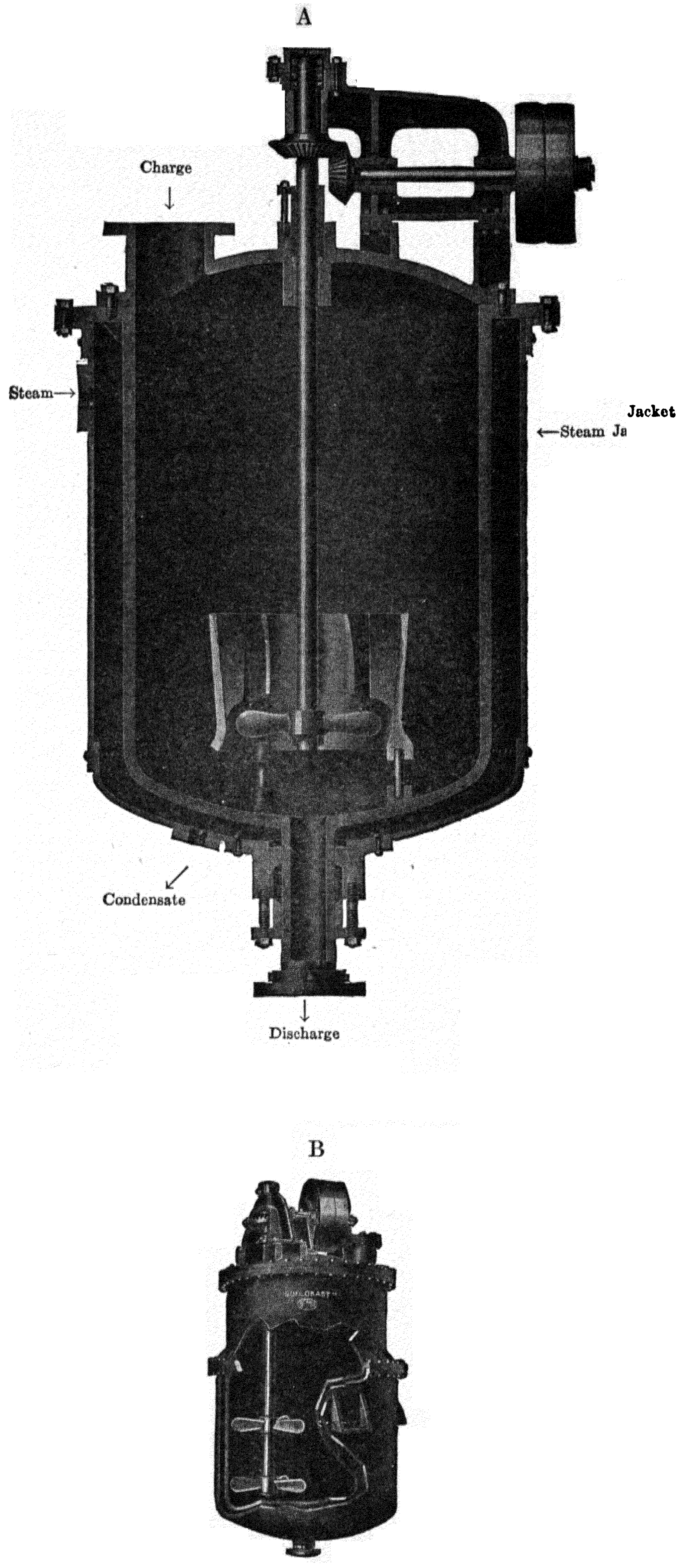

Fig. 66.—Sulfonators

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EXPT. 34. SODIUM BENZENESULFONATE

1. Why is the benzene added in small portions to the fuming H_2SO_4?

2. Why is the reaction mixture poured into NaCl solution?

3. Write the equations for the preparation of sodium benzenesulfonate.

4. Explain the formation of diphenylsulfone in the preparation of sodium benzenesulfonate.

5. How does scratching the side of the beaker aid crystallization?

6. Why is the sodium benzenesulfonate washed with a saturated NaCl solution?

7. Write the equations for the formation of lead and zinc benzenesulfonates.

8. Write the equation for the preparation of benzenesulfonyl chloride.

9. Write the equation for the preparation of benzenesulfonamide.

10. What is the importance of the last two reactions?

11. Outline the scheme used to separate the excess H_2SO_4 from the sulfonic acid.

What other compounds may be used instead of $BaCO_3$?

12. What is the purpose of the baffle plate surrounding the stirrer shown in Fig. 66A?

13. What important factors determine the degree of sulfonation?

14. What classes of compounds are made from sulfonic acids?

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NITRATION OF AN AROMATIC HYDROCARBON

EXPT. 35. NITROBENZENE

Preparation.

To 150 g. of conc. H_2SO_4 in a 500 cc. flask add slowly and with constant shaking 100 g. of conc. HNO_3. Cool the mixture to room temperature and add 50 cc. of benzene in portions of 2 cc. each, shaking thoroughly after each addition. During this operation the temperature should be kept at 50°–60°. After all the benzene has been added attach a condenser. Heat in a water bath for 1 hour at 60° (temperature of the water) with occasional shaking. (Continue with the next step immediately, otherwise on standing a considerable amount of *m*-dinitrobenzene will be produced.) Cool, transfer the liquid to a separatory funnel, wait for the separation of the layers and draw off the lower layer (mixture of nitric and sulfuric acids). Shake the remaining liquid (nitrobenzene) with 30 cc. of water. Separate the lower layer (nitrobenzene) and shake it again with an excess of a 5 per cent Na_2CO_3 solution until an alkaline solution is shown with litmus paper. Separate and then shake again with 30 cc. of water. Separate the nitrobenzene layer and allow it to flow into a dry flask. Add 4 g. of anhydrous calcium chloride and warm on a water bath until the turbid liquid becomes clear. Transfer it to a dry 200 cc. distilling flask with a low side-arm and distill on a wire gauze, using an air condenser. Collect the fraction distilling between 205°–208°. B.p. of nitrobenzene is 208°. **Stop the distillation when about 1 cc. of the liquid remains in the distilling flask.**

Yield = g. Calculated = g. Percentage yield =

Note the odor of nitrobenzene.

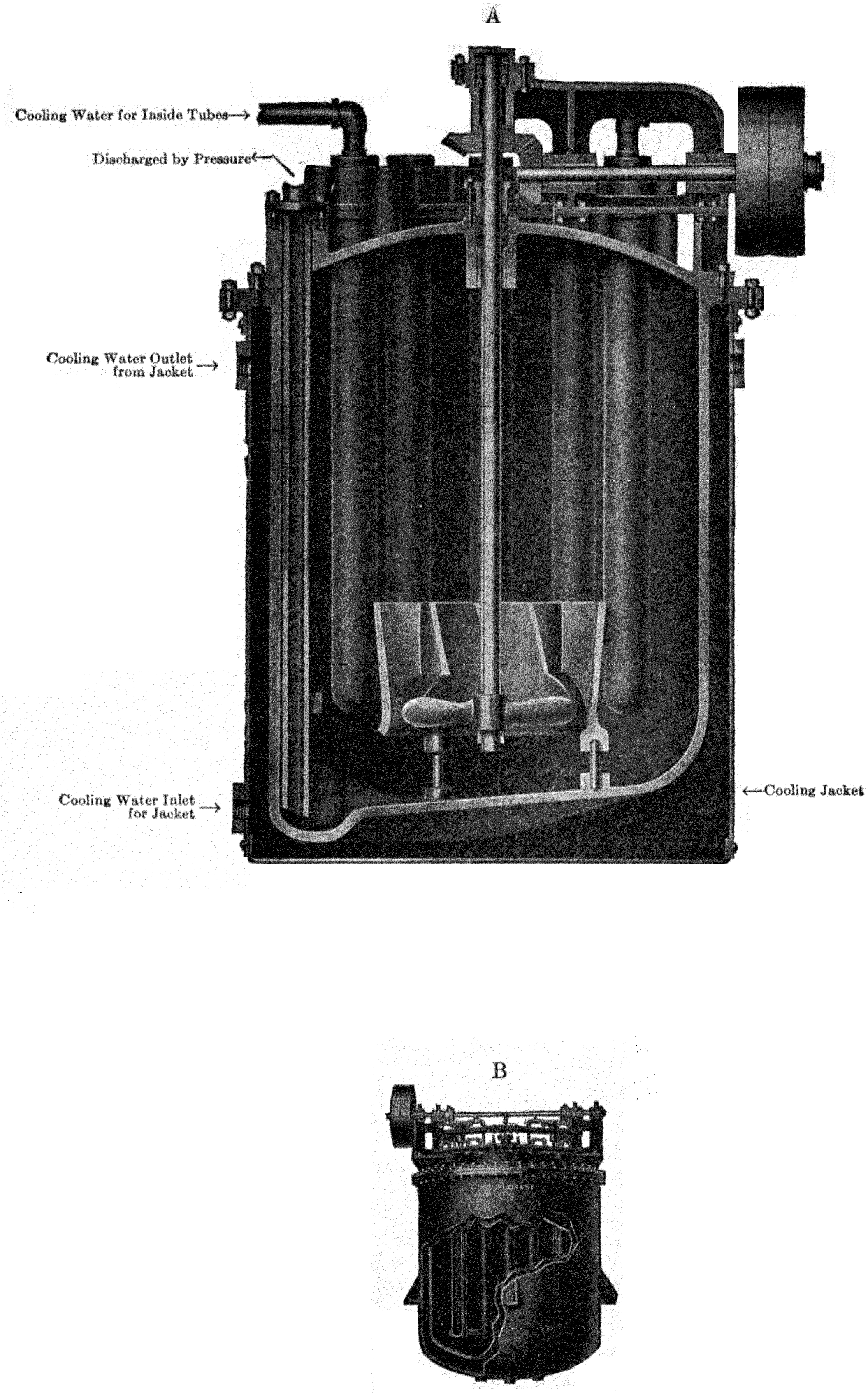
A
Cooling Water for Inside Tubes
Discharged by Pressure
Cooling Water Outlet from Jacket
Cooling Water Inlet for Jacket
Cooling Jacket
B

FIG. 67.—Nitrators.

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EXPT. 35. NITROBENZENE

1. Write the equation for the preparation of nitrobenzene.

2. What is the function of the H_2SO_4 in this experiment?.

3. Why is the temperature kept at 50°–60°?

4. Why are the reagents for the washing of the nitrobenzene used in the order specified?

5. Why is a distilling flask with a low side-arm used in the final distillation?

6. What name is given to the mixture of H_2SO_4 and HNO_3?

7. Why do you stop the distillation before dryness is reached?

8. State the uses of nitrobenzene.

9. **What important factors determine the degree of nitration?**

10. What important class of compounds is made from nitro compounds?

11. Why are many cooling tubes necessary in the nitrators shown in Fig. 67?

12. Compare the relative reactivities of aliphatic hydrocarbons and aromatic hydrocarbons when treated with "mixed acids."

13. Write formulas and names of all the reduction products of nitrobenzene.

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REDUCTION OF A NITRO COMPOUND TO AN AMINE

EXPT. 36. ANILINE

Preparation.

Warning:—*Aniline is poisonous. Do not breathe the vapor, and keep it off your hands.*

To 60 g. of **iron powder** in a 1-liter round-bottom flask add 80 cc. of water and shake vigorously. Weigh 50 g. of nitrobenzene. Warm the flask to about 70° and add 5 drops of the nitrobenzene. Now pour into the flask 5 cc. of conc. HCl and, in portions of about 3 cc., the remainder of the nitrobenzene. After each addition of the nitrobenzene shake thoroughly and cool so that the temperature of the mixture in the flask is kept at 80°–90°. When all the nitrobenzene has been added and the temperature no longer rises on shaking, attach a reflux condenser and heat the mixture on a water bath for $\frac{1}{2}$ hour. Distill the mixture with steam (see p. 45). It is not necessary to make the mixture alkaline since no free HCl is present to combine with the aniline. As soon as the distillate no longer has a milky appearance, stop the distillation, transfer the distillate to a separatory funnel, allow to settle, and draw off the lower layer (aniline). Saturate the water remaining in the funnel with NaCl, allow it to stand for 1 hour and draw off the lower layer and discard. The liquid (aniline) remaining in the funnel is poured into the portion of aniline previously separated. Distill, reject the first 5 cc. which contains water. Collect the fraction distilling over between 183°–186°. The boiling point of aniline is 184.7°.

Yield = g. Calculated = g. Percentage yield =

Properties.

(*a*) **Test with Indicator Papers.**—To 10 cc. of water add 1 cc. of aniline and shake. Test with litmus papers. **Results**:—

Repeat with Congo red paper, which has been moistened with dilute HCl. **Result**:—

(*b*) **Basic Property of Aniline.**—Shake 1 cc. of aniline with 10 cc. of water. Pour off the supernatant liquid and add to it 1 cc. of a 10 per cent ferric chloride solution. **Result**:—

(*c*) **Aniline and Acids.**—To 5 cc. of aniline on a watch glass add, with stirring, 5 cc. of conc. HCl, drop by drop. **Result**:—

Dry the crystals on a steam bath for a few hours.

Dissolve 2 g. of the aniline hydrochloride in 5 cc. of water and add 5 cc. of a 10 per cent NaOH solution. **Result**:—

Dissolve 1 g. of aniline hydrochloride in 5 cc. of water and test with litmus paper. **Result**:—

(*d*) **Acetanilide.**—To 1 cc. of aniline in a 20 cm. test tube add 3 cc. of acetic anhydride, drop by drop, and boil for 2 minutes. Cool, add 5 cc. of water and heat until a clear solution results. Cool well and shake vigorously. Filter by suction and wash the residue with 5 cc. of cold water. Dry on a porous plate.

To about 0.5 g. of the prepared acetanilide add 5 cc. of conc. HCl. Boil on a water bath for 30 minutes. Then cool in an ice bath. **Result**:—

Make alkaline with a 40 per cent NaOH solution. **Result**:—

(*e*) **Sulfanilic Acid.**—Pour 15 g. of aniline into a 100 cc. round-bottom flask, add slowly and with constant stirring 50 g. of conc. H_2SO_4. **Result**:—

Heat the mixture in an oil bath at 180°–190° for 4–5 hours. To test for the completion of the sulfonation, add 2 drops of the reaction mixture to a few drops of strong NaOH solution. If no oily drops of aniline separate, the reaction is considered completed. Carefully pour the product into 200 cc. of cold water. Filter by suction, and wash the precipitate with cold water. Dissolve the residue in boiling water, add very slowly 5 g. of animal charcoal and continue boiling for 10 minutes; filter while hot, and set the solution aside to crystallize. Filter off the crystals and dry.

(*f*) **Aniline and Nitrous Acid.**—Refer to Expt. (*a*) (p. 147).

(*g*) **Aniline Black.**—Place 2 g. of aniline hydrochloride, 1 g. of $KClO_3$, 2 g. of powdered $CuSO_4$ and 0.8 g. of NH_4Cl in a 100 cc. beaker. Add 50 cc. of water and stir. Slowly heat to 70° on a water bath and keep at this temperature for 10 minutes. Cool. **Result:**—

(*h*) **Color Reactions.**—1. Aniline and bleaching powder: Shake 1 drop of aniline with 5 cc. of water and add 2 cc. of a filtered bleaching powder solution. **Result:**—

2. Aniline and $K_2Cr_2O_7$: On a watch glass stir together 2 drops of aniline and 5 drops of conc. H_2SO_4. Then add 5 drops of a 10 per cent $K_2Cr_2O_7$ solution. **Result:**—

(*i*) **Effect of Light.**—Expose 5 cc. of freshly prepared aniline to light until the next laboratory period. **Result:**—

(*j*) **Dimethylaniline and Nitrous Acid.**—To 1 cc. of dimethylaniline in a 20 cm. test tube add 4 cc. of HCl (1 : 1) solution with constant shaking. **Result:**—

Cool the solution in ice and add a cold solution of $NaNO_2$ (about 0.5 g. in 5 cc. of water). **Result:**—

This compound is *p*-nitrosodimethylaniline hydrochloride. Treat the yellow product with 15 cc. of 10 per cent NaOH solution. **Result:**—

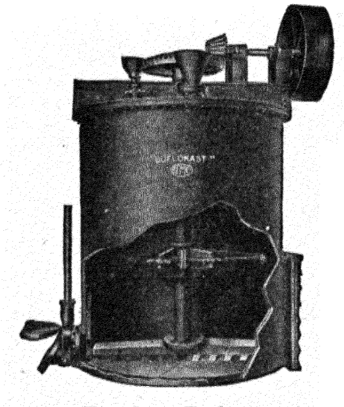

Fig. 68.—Reducer.

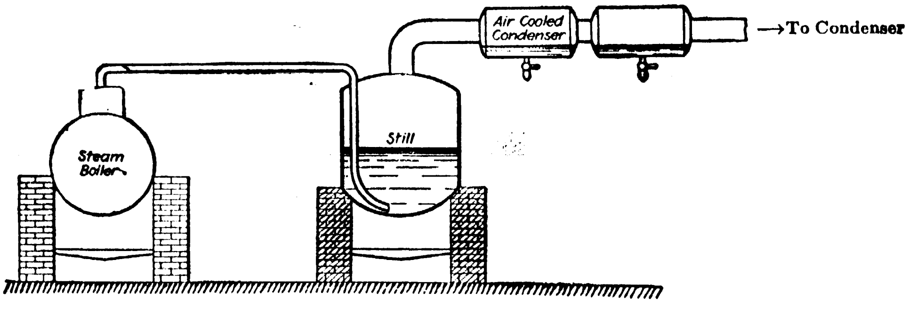

Fig. 69.—Industrial Steam Distillation.

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EXPT. 36. ANILINE

1. Write the equations for the preparation of aniline by the method which you used?

2. What is actually the reducing agent in this method of preparation?

3, Mention other reagents that may be used to reduce nitrobenzene to aniline.

4. Why does aniline show basic properties?

5. Write the equations for the reactions in Expt. (*c*) and name the products.

6. Write the equations for the reactions in Expt. (*d*).

7. What reagents could be used in Expt. (*d*) instead of acetic anhydride?

8. Write the equations for the reactions involved in Expt. (*e*).

9. Write the equations for the reactions in Expt. (*f*) and name the products.

10. Mention the uses of aniline black.

11. What type of reagent is used in the color tests for aniline?

12. Write the equations for the reactions in Expt. (*j*).

Do aliphatic tertiary amines give similar products?

13. What reagents are used for the reduction of nitro compounds to amino compounds?

14. Name some important uses for aniline.

15. Compare the chemical properties of aniline and benzylamine. Give equations.

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REACTIONS OF DIAZO OR DIAZONIUM COMPOUNDS

EXPT. 37. REACTIONS OF DIAZOTIZED ANILINE

(*a*) **Preparation of Benzenediazonium Chloride.**—To 30 g. of aniline in a liter beaker add 150 g. of conc. HCl and 550 cc. of water. Stir and cool the mixture to 0°–2° in a salt-ice bath. (To aid cooling, put small pieces of ice in the beaker.) Pour into a dropping funnel a solution of 25.5 g. of sodium nitrite dissolved in 80 cc. of water. Arrange the funnel so that the stem dips below the surface of the liquid in the beaker. Then slowly add the contents of the funnel to the solution in the beaker, stirring constantly. (To aid cooling, put small pieces of ice in the beaker.) Continue the addition until, near the end of the addition, a test portion of the solution gives a blue color with starch iodide paper. This solution is to be used in the experiments outlined below. It must be kept in the ice bath until all the experiments are completed.

(*b*) **Preparation of Phenol.**—Introduce 100 cc. of the diazotized aniline solution into a 200 cc. distilling flask connected with a condenser and warm at 60° on a water bath until the evolution of nitrogen ceases. Then distill on a wire gauze about 70 cc. and extract the phenol from the distillate with ether. The phenol can be identified by the reaction given under phenol. Expts. (*e* and *l*) (pp. 151 and 152).

(*c*) **Preparation of Benzene.**—To 150 cc. of the diazotized aniline solution in a 500 cc. beaker add a solution of 10 g. of NaOH in 30 cc. of water. Cool to 0° in an ice bath. Now make a solution of 20 g. of stannous chloride in 50 cc. of water and with constant stirring add a 50 per cent solution of NaOH until the precipitate which forms first is redissolved in an excess of the NaOH. Cool this latter solution in an ice bath and add it in portions of 5 cc. to the ice-cold benzenediazonium chloride solution. After each addition wait until the evolution of nitrogen has stopped before adding more. Then transfer the contents of the beaker to a distilling flask and distill over about 20 cc. Note the odor of the distillate. What is present in the distillate?

(*d*) **Preparation of Iodobenzene.**—To 100 cc. of the diazotized aniline solution gradually add, with constant stirring, a solution of 6 g. of potassium iodide dissolved in 15 cc. of water. Keep the mixture in an ice bath until all the potassium iodide solution has been added. Then heat on a water bath at about 60° until the evolution of nitrogen ceases. The heavy dark oil which separates is iodobenzene.

(*e*) **Preparation of Chlorobenzene (Sandmeyer's reaction).**—Prepare a 10 per cent cuprous chloride solution as follows: To 5 g. of $CuSO_4$ add 3 g. of NaCl in 10 cc. of water. Heat to boiling and then add 20 g. of conc. HCl and 3 g. of copper filings or foil and continue heating until the solution becomes clear. Then add conc. HCl until the total weight is 40 g.

$$CuSO_4 + 2NaCl \rightarrow CuCl_2 + Na_2SO_4$$
$$CuCl_2 + Cu \rightarrow 2CuCl$$

Pour 100 cc. of the diazotized aniline solution into a 300 cc. flask. Add 20 g. of the cold cuprous chloride solution slowly and with constant stirring. Attach a reflux condenser and heat to boiling until the evolution of nitrogen ceases. The chlorobenzene separates out as an oil.

(*f*) **Preparation of Chlorobenzene (Gattermann's reaction).**—Prepare some finely divided copper as follows: Dissolve 10 g. of copper sulfate in 40 cc. of water. Cool, and sift about 4 g. of zinc dust into the solution until it is decolorized. Wash the precipitated copper 3 times with water by decantation and then add 10 per cent HCl to dissolve any zinc remaining. Allow to stand for 30 minutes and stir frequently. Filter by suction and wash well with water. To prevent oxidation, keep the copper moist.

To 100 cc. of the diazotized aniline solution gradually add the copper prepared as above. After the evolution of nitrogen has ceased, reflux for 30 minutes. The chlorobenzene separates as an oil. Cool and extract with ether. Recover the chlorobenzene.

(*g*) **Preparation of Phenylhydrazine.**—

Warning:—*Phenylhydrazine is poisonous. Do not breathe its vapors, and keep it off your hands.*

Dissolve 25 g. of stannous chloride in 20 cc. of conc. HCl and cool. Pour this slowly, with constant stirring, into 100 cc. of the diazotized aniline solution (kept cool with ice). **Result:**—

$$C_6H_5N_2Cl + 2SnCl_2 + 4HCl \rightarrow C_6H_5NH \cdot NH_2 \cdot HCl + SnCl_4$$

The precipitate formed is phenylhydrazine hydrochloride. Filter by suction. Transfer the residue to a small separatory funnel and add 10 cc. of water and a few cubic centimeters of NaOH solution (1 : 10). Shake. The resulting mixture should show an alkaline reaction. Note the oily layer of phenylhydrazine. Extract the oil with ether. Allow the ethereal solution to evaporate on a watch glass in the hood. **Result:**—

Add a few drops of conc. HCl to the liquid on the watch glass. **Result:**—

For reactions of phenylhydrazine see Expts. (*f*) (p. 68); (*e*) (p. 119).

(*h*) **Preparation of Diazoaminobenzene.**—To 40 cc. of the diazotized aniline solution add gradually, and with constant stirring, an ice-cold solution of 2.5 g. of aniline hydrochloride in 10 cc. of water. Then add 10 g. of sodium acetate dissolved in just enough water to take it into solution, and stir. After standing for an hour, filter with suction and wash the residue with a small amount of water. Dry on a porous plate.

(*i*) **Preparation of *p*-aminoazobenzene.**—To 1 g. of powdered dry diazoaminobenzene add 0.5 g. of powdered aniline hydrochloride. Mix thoroughly. Put this mixture in a large test tube and add 2.5 g. of aniline. Heat in a water bath for 1 hour at 45°. Stir frequently. Add 40 cc. of dilute acetic acid (10 per cent). Stir until the undissolved precipitate completely solidifies. Filter and wash the precipitate with a small amount of water. Transfer the precipitate to a beaker, add 150 cc. of water, and heat. When a temperature of 50° is reached add 10 cc. of conc. HCl. Boil for 3 minutes and filter the boiling solution. The steel-blue, needle-like crystals which separate on cooling are *p*-aminoazobenzene hydrochloride.

(*j*) **"Coupling" with Phenol.**—(See warning on p. 151.) Dissolve about 0.5 g. of phenol in 10 cc. of 10 per cent NaOH solution. To this solution add with stirring 10 cc. of the cold diazotized aniline solution. **Result:**—

(*k*) **"Coupling" with Dimethylaniline.**—Add 10 drops of conc. HCl to 10 drops of dimethylaniline. Shake. Dilute with 20 cc. of water. To this solution add 10 cc. of the cold diazotized aniline solution. **Result:**—

the mixture alkaline with a 10 per cent NaOH solution. **Result:**—

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EXPT. 37. REACTIONS OF DIAZOTIZED ANILINE

1. **Write the equations for the reactions in Expt. (*a*).**

2. **Why must the mixture be cooled in the preparation of a diazonium compound?**

3. **Explain all the reactions which take place and which finally result in the blue color with the starch iodide paper.**

4. **Why must the solution be thoroughly stirred before you test with the starch iodide paper?**

5. **Why must the diazotized aniline solution be kept in an ice bath until all the experiments are completed?**

What compound would be formed if the temperature were increased?

6. **Why should the funnel dip below the surface of the liquid during the addition of the $NaNO_2$ solution?**

7. **What are the three functions of the HCl in Expt. (*a*)?**

8. **Write the equation for the reaction in Expt. (*b*).**

9. **Write the equations for the reactions in Expt. (*c*).**

10. Write the equation for the reaction in Expt. (*d*).

11. What is the function of the cuprous chloride in Expt. (*e*)?

12. Write the equation for the preparation of chlorobenzene in Expt. (*e*).

13. What is the function of the finely divided copper in Expt. (*f*)?

14. Write the equations for the reactions in Expt. (*g*).

15. Write the equations for the reactions in Expt. (*h*).

16. What is the function of the sodium acetate in Expt. (*h*)?

17. Write the equations for the reactions in Expt. (*i*).

18. Write the equations for the reactions in Expts. (*j*) and (*k*).

19. To what two general types of reactions do diazonium compounds respond?

Illustrate.

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CONVERSION OF A SULFONIC ACID INTO A PHENOL

EXPT. 38. PHENOL

Preparation.

Warning:—*Do not allow phenol to come in contact with the skin. It produces painful wounds.*

Support an iron crucible (if not available use a porcelain crucible) RIGIDLY in a triangle or on an iron ring. Introduce 4 g. of solid NaOH and 1 cc. of water. (Protect your hands with gloves or cloth and wear goggles.) Gently heat until the NaOH has liquefied and then add 2 g. of powdered sodium benzenesulfonate. In heating hold the burner so that the hand is never under the crucible. Continue heating to about 250°. (Protect the bulb of your thermometer by encasing it in copper foil.) Stir constantly. Do not char. When this temperature has been reached a low flame should be used. This will be sufficient to keep the melt at the required temperature. After 15 minutes heating, remove the flame, allow the melt to cool, and dissolve it in 25 cc. of water. Slowly acidify with HCl (1 : 1). Extract twice with ether the yellow oil (phenol) which separates. Allow the ether to evaporate on a watch glass. Note the odor of the residue and test as in Expts. (*e*) and (*l*).

Properties. (Use phenol furnished by the stock room.)

(*a*) **Odor.**—Note the odor of phenol.

(*b*) **Solubility.**—Test the solubility of phenol in water, benzene, alcohol and ether. **Results:**—

(*c*) **Acidity.**—Dissolve a few crystals of phenol in 10 cc. of water. Test the solution with blue litmus paper. **Result:**—

(*d*) **Sodium Phenolate.**—To 10 cc. of water add 3 g. of phenol and shake. Some of the phenol dissolves. Now add 40 per cent NaOH solution, drop by drop, until all the phenol dissolves. Divide the solution into two parts. To one part add 5 cc. of 40 per cent H_2SO_4. Pass carbon dioxide from a Kipp generator through the other portion. **Results:**—

(*e*) **Tribromophenol.**—To 5 cc. of a 2 per cent solution of phenol in water add bromine water, drop by drop, until a faint yellow color persists. Note the color of the precipitate:—

(*f*) **Phenolsulfonic Acids.**—To about 1 g. of phenol in a test tube add 4 cc. of conc. H_2SO_4. Shake. Heat in a boiling water bath for 1 hour. Cool and pour contents slowly into 10 cc. of water. The resulting solution contains phenolsulfonic acids.

(*g*) *o*- **and** *p*-**nitrophenols.**—Put 3 g. of phenol in a test tube and heat in a water bath until it liquefies. Then add it slowly and with constant stirring to a solution of 4 cc. of conc. HNO_3 in 15 cc. of water. During this operation the temperature of the mixture should be kept at 30°. Set the mixture aside until the next laboratory period. Note the heavy dark oil which separates. This is a mixture of *o*- and *p*-nitrophenol. These two compounds may be separated by steam distillation, only the *o*-compound is volatile with steam.

(*h*) **Picric Acid.**—In a test tube stir and bring to a boil 3 g. of phenol and 3 g. of conc. H_2SO_4. Cool, and under the hood add this solution slowly, drop by drop and with constant agitation, to 9 cc. of conc. HNO_3 in a 20 cm. test tube. Then shake vigorously for 15 minutes longer. When red fumes are no longer evolved, add 2 cc. of fuming nitric acid and heat the solution on a water bath for 30 minutes. Then slowly pour the solution into cold water. Boil the mixture and allow to cool. **Result:**—

(*i*) **Formation of Anisole.**—**Warning:**—*Do not breathe dimethyl sulfate. Its vapors are poisonous.* To 2 g. of phenol in a 20 cm. test tube add 2 cc. of dimethyl sulfate. Mix thoroughly and pour 8 cc. of a 10 per cent

NaOH solution into the mixture. Heat on a boiling water bath for 10 minutes and shake. Cool and add 10 cc. of 10 per cent NaOH solution. Extract with 20 cc. of ether. Allow the ether to evaporate and note the odor of the residue. **Result:—**

(*j*) **Formation of Phenyl Acetate.**—To 1 g. of phenol add acetyl chloride, drop by drop, until a reaction is no longer evident. Pour the mixture into 5 cc. of water. Note the odor of the liquid which separates:—

(*k*) **Color Reactions.**—Ferric chloride: To 3 cc. of a 2 per cent solution of phenol add 2 drops of ferric chloride solution (5 per cent). **Result:—**

Add 1 cc. of 10 per cent HCl. **Result:—**

(*l*) **Phenolphthalein.**—To a mixture of 0.5 g. of phenol and 0.5 g. of phthalic anhydride in a test tube add 10 drops of conc. H_2SO_4. Shake. Heat for 5 minutes at 160° on a sand or oil bath. Cool. Add slowly 10 cc. of water and shake. Cool. Add with constant shaking enough 10 per cent NaOH solution to give a permanent pink color. Pour the contents of the tube into 100 cc. of water and make the solution acid, then alkaline. **Results:—**

(*m*) **Formation of Resins.**—Place 5 cc. of formalin and 5 cc. of ammonium hydroxide in a small evaporating dish. Stir. Evaporate the mixture to dryness on a water bath. Weigh the hexamethylenetetramine product and transfer it to a crucible. Add an equal weight of phenol. Mix thoroughly. Heat gently on an asbestos pad. Do not char. Allow to cool. **Result:—**

(*n*) **Saponified Cresol Solution for Disinfection.**—Heat 30 g. of linseed oil in a beaker to 70° in a water bath. Dissolve 8 g. of KOH in 5 cc. of water and add it to the hot linseed oil. Mix thoroughly. Add 3 cc. of alcohol and stir. Heat the mixture without stirring at 70° until a small portion is found to be soluble in boiling water without the separation of oily drops. Add 50 g. of cresol and mix thoroughly. Heat at 70° until a clear solution is obtained. A 1–3 per cent solution of this can be used as a disinfectant.

(*o*) **Fluorescein.**—Grind together 7.5 g. of phthalic anhydride and 11 g. of resorcinol. Transfer to a nickel or iron crucible. Heat in an oil bath to 180° and stir. During 5 minutes add in small portions 4 g. of powdered fused zinc chloride and stir continuously. Continue stirring and raise the temperature to 210°. Maintain this temperature until the liquid, which gradually thickens, becomes solid. Cool and remove the mass from the crucible by means of a knife (use goggles). Pulverize and boil for 10 minutes in about 150 cc. of 5 per cent HCl. Filter off the fluorescein, wash free of acid and dry. **Result:—**

Dissolve small amounts in alcohol and in NaOH solution. **Results:—**

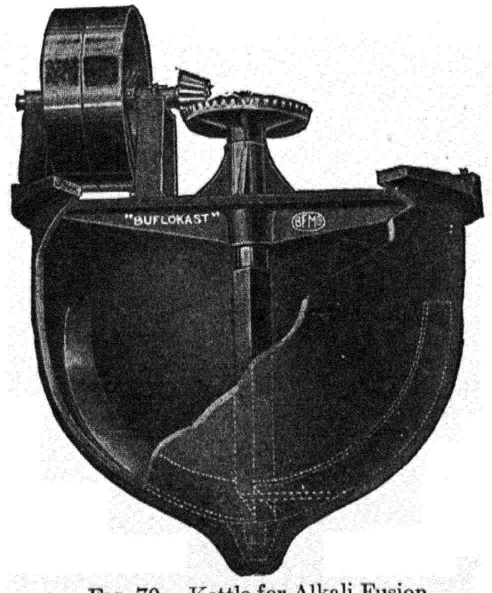

Fig. 70.—Kettle for Alkali Fusion.

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EXPT. 38. PHENOL

1. Write the equations for the preparation of phenol as given in this experiment.

2. Why should you use an iron crucible in preference to a porcelain one?

3. Mention several examples of organic compounds which do not contain a carboxyl group but show acid properties.

4. Write the equations for the reactions in Expt. (*d*).

Which is the stronger acid, carbonic or carbolic?

Upon what experimental evidence do you base your answer?

Which is the corrosive acid?

5. Write the equation for the reaction in Expt. (*e*).

6. Write the equations for the reactions in Expt. (*f*).

7. Write the equations for the reactions in Expt. (*g*).

What would form if the temperature or the concentration of the acid were increased?

8. Write the equations for the reactions in Expt. (*h*).

9. Why is phenol treated with concentrated H_2SO_4 at the beginning of Expt. (*h*)?

10. Write the equations for the reactions in Expt. (*i*).

11. Write the equation for the reaction in Expt. (*j*).

To what is the odor due?

12. Write the equations for the reactions in Expt. (*l*).

What is the function of the H_2SO_4?

13. What is the name of the commercial product made by a method similar to the one shown in Expt. (*m*)?

State the uses for the product.

14. Name several commercial products analogous in composition to the product prepared in Expt. (*n*).

15. What metal is used in the construction of kettles for alkali fusions? (Fig. 70.)

16. Write the equations for the reactions in Expt. (*o*).

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EXPT. 39. BENZALDEHYDE

Properties.

(*a*) **Odor.**—Note the odor of benzaldehyde.

(*b*) **Solubility.**—Test the solubility of benzaldehyde in alcohol, ether and water. **Results:**—

(*c*) **Oxidation.**—On a small watch glass expose 5 drops of benzaldehyde for about two hours. **Result:**—

(*d*) **Aldehyde Reactions.**—Repeat the following experiments with benzaldehyde and note your results.

Experiments.	Results.		Formula of Compound Produced with Benzaldehyde.
	With Benzaldehyde.	With Acetaldehyde.	
16. (*g*) (p. 63)			
16. (*d*) (p. 68)			
16. (*e*) (p. 68)			
16. (*f*) (p. 68)			

(*e*) **Benzaldehyde and Aniline.**—Add 2.3 g. of benzaldehyde to 2 g. of aniline in a small test tube. Shake and heat in an oil bath for 3 hours at 125°. While still hot pour slowly into 25 cc. of ice water and agitate. **Result:**—

Allow to stand until the next laboratory period. **Result:**—

(*f*) **Benzaldehyde and Ammonia.**—To 10 drops of benzaldehyde in a test tube add 3 cc. of ammonium hydroxide. Shake, stopper the tube, and set aside until the next laboratory period. **Result:**—

(*g*) **Benzaldehyde and Sodium Hydroxide (Cannizzaro's reaction).**—To 8 g. of benzaldehyde add a solution of 7 g. of NaOH in 5 cc. of water. Shake until a permanent emulsion is formed. Allow to stand for 10 minutes, stopper and set aside until the next laboratory period. Dissolve the solid which forms in a little water and extract the mixture twice with ether. Acidify the aqueous portion with HCl. Benzoic acid is precipitated. Allow the ether portion to evaporate. The residue is benzyl alcohol.

(*h*) **Formation of Benzoin.**—In a 20 cm. test tube shake a solution of 5 g. of benzaldehyde in 6 cc. of alcohol and a solution of 0.5 g. of potassium cyanide (*poison*) in 5 cc. of water. Attach a reflux condenser and heat for 20 minutes on a water bath. Cool in ice-water. **Result:**—

(*i*) **Formation of *m*-nitrobenzaldehyde.**—To 20 cc. of conc. H_2SO_4 in a small flask add, drop by drop, 2 cc. of fuming nitric acid. Shake. Place the flask in a freezing mixture and cool it to 0°. Add, very slowly and with constant agitation, 5 g. of benzaldehyde. Do not allow the temperature to rise above 5°. When this operation is completed, warm the flask in a water bath until the temperature reaches 40°. Cool, and pour the mixture on cracked ice in a small beaker. **Result:—**

(*j*) **Formation of Cinnamic Acid (Perkin's reaction).**—Into a 100 cc. flask introduce 10 g. of benzaldehyde, 15 g. of acetic anhydride, and 5 g. of finely powdered, freshly fused sodium acetate. Shake well. Attach a reflux condenser with a $CaCl_2$ drying tube. Heat in an oil bath for 8 hours at 180°. **Pour the reaction product into 100 cc. of water and stir.** Impure cinnamic acid crystals separate. A small amount of excess benzaldehyde is also present. This may be eliminated by subjecting the mixture to steam distillation. The impure cinnamic acid may be purified by recrystallization from water.

NOTE:—For the reaction of benzaldehyde in the preparation of malachite green, see p. 163.

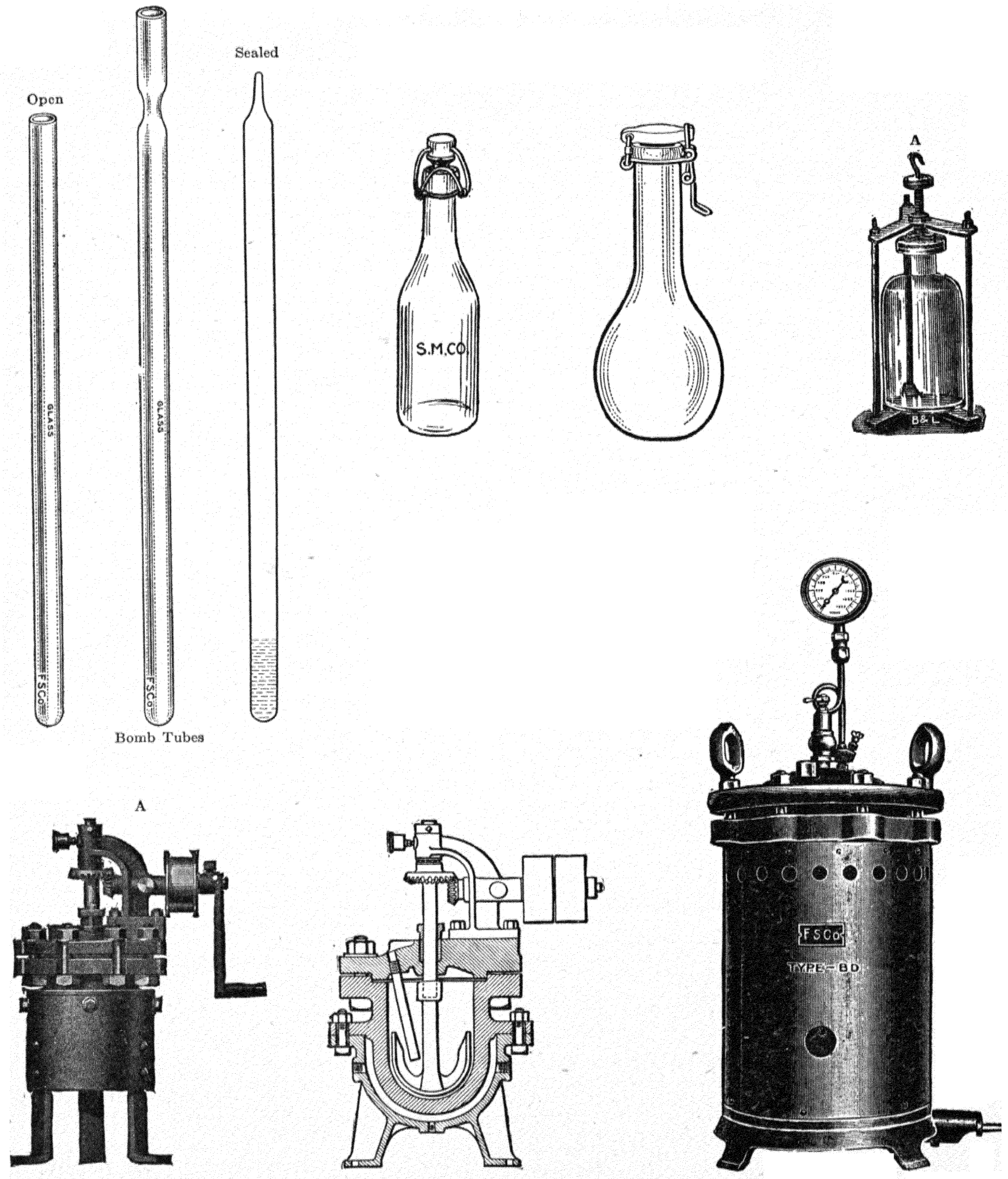

FIG. 71.—Equipment for Reactions under Pressure—Autoclaves.

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EXPT. 39. BENZALDEHYDE

1. Write the equations for the reactions in Expt. (*c*).

2. Write the equation for the reaction in Expt. (*e*).

3. Write the equation for the reaction in Expt. (*f*).

What compound would be formed by the action of ammonia on acetaldehyde?

4. Write the equations for the reactions in Expt. (*g*).

Is there an analogous reaction with (*a*) acetaldehyde and (*b*) formaldehyde?

5. Write the equation for the reaction in Expt. (*h*).

What is the function of the KCN solution?

6. Write the equation for the reaction in Expt. (*i*).

Why is the nitration conducted at low temperature?

What reaction would take place with dilute HNO_3?

7. Write the equations for the reactions in Expt. (*j*).

What is the function of the sodium acetate?

What is the function of the acetic anhydride?

8. What type of experiment is conducted in bomb tubes? *

9. What apparatus would you use in the laboratory to heat substances at temperatures above their boiling points?

10. Write equations for some reactions which are performed in autoclaves or bomb tubes.

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EXPT. 40. NAPHTHALENE, ANTHRACENE AND THEIR DERIVATIVES

NAPHTHALENE

Properties.

(*a*) **Odor.**—Note the odor of naphthalene.

(*b*) **Solubility.**—Test the solubility of naphthalene in water, alcohol and ether. **Results:**—

(*c*) **Sublimation.**—Refer to Expt. (*d*) (p. 7).

(*d*) **Formation of Naphthalene Picrate.**—Dissolve 0.2 g. of naphthalene in 10 cc. of boiling alcohol. Add 0.3 g. of picric acid and heat to boiling in a water bath. Allow to cool. **Result:**—

(*e*) **Formation of α-nitronaphthalene.**—To 10 g. of powdered naphthalene add, slowly and with constant stirring, a cold mixture of 6 cc. of conc. H_2SO_4 and 6 cc. of conc. HNO_3. Do not allow the temperature to rise above 20°. Allow to stand for 2 hours. Then pour the contents of the tube into 50 cc. of cold water. The precipitate which separates contains α-nitronaphthalene, a small amount of dinitronaphthalene, and some unchanged naphthalene. The last named compound may be removed by steam distillation.

(*f*) **Formation of α-bromonaphthalene.**—To 0.2 g. of powdered naphthalene add 2 drops of bromine. Blow over the mouth of the tube. **Result:**—

Pour the contents of the tube into water. **Result:**—

(*g*) **Formation of Sodium β-naphthalenesulfonate.**—Pour 5 cc. of conc. H_2SO_4 into a 20 cm. test tube and heat to 50°. Add gradually (in portions of 1 g.) 7 g. of powdered naphthalene. Shake after each addition. Heat the tube in an oil bath at a temperature of 160° for 3 hours. Then pour the reaction product into a beaker containing 100 cc. of water. Filter off the excess naphthalene and add to the filtrate, with constant stirring, powdered calcium carbonate until no more carbon dioxide is evolved. Filter through muslin and evaporate the solution to one-half its volume. Filter again through a filter paper. To the filtrate add a strong solution of sodium carbonate until a precipitate is no longer formed. Filter first through muslin and then through filter paper. Evaporate the filtrate almost to dryness on a water bath and set aside. **Result:**—

(*h*) **Formation of β-naphthol from Sodium β-naphthalenesulfonate.**—Put 6 g. of sodium hydroxide in an iron crucible placed RIGIDLY in a triangle. Add 1 cc. of water and heat to 280°, observing the same precautions as in Expt. 38 (p. 151). When this temperature is reached, lower the flame and add 2 g. of sodium β-naphthalenesulfonate in small portions and with constant stirring. After each addition the temperature falls somewhat. Do not add any more of the salt until the temperature reaches 280° again. When all the sulfonate has been added, raise the temperature to 310°. Hold at this temperature for 5 minutes. Allow to cool. Dissolve the solid mass in boiling water and cool. Acidify the solution with HCl (1 : 1). Cool. The β-naphthol is precipitated. It can be recrystallized from ether.

(*i*) **Color Reaction of β-naphthol.**—Repeat Expt. (*k*) (p. 152). **Result:**—

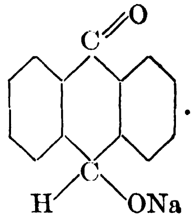
ANTHRACENE

Properties.

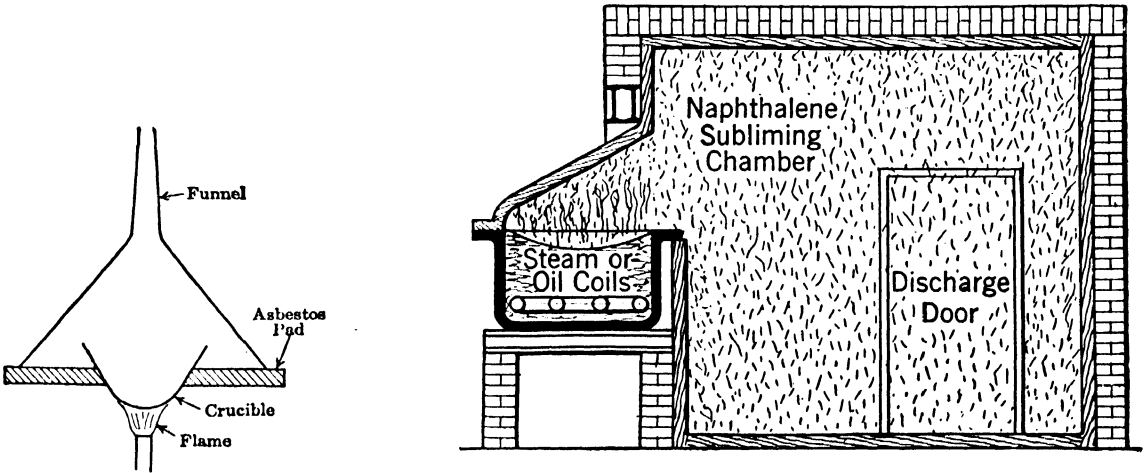
(*j*) **Sublimation.**—Sublime about 0.2 g. of anthracene as in Expt. (*d*) (p. 7). **Result:**—

(*k*) **Formation of Anthraquinone.**—Into a 1 liter round-bottom flask introduce 20 g. of powdered phthalic anhydride, 80 g. of benzene and 40 g. of powdered or pea-size dry $AlCl_3$. Attach a reflux condenser and gradually heat on a water bath. Shake vigorously or use mechanical agitation. If the reaction becomes too violent, cool the flask. Gradually increase the temperature to 65° and maintain this temperature until no more HCl is evolved. Cool and remove the condenser. Add *slowly* and with continuous agitation 200 cc. of ice-water. Steam distill the excess of benzene. Cool and discard the supernatant liquid being careful not to discard the solid material. Add 300 cc. of water to the residue in the flask. Add 30 g. of sodium carbonate. Shake and heat on an asbestos pad. Boil *gently* for 1 hour with occasional shaking and stirring with a glass rod. Filter the hot solution through a Büchner funnel and wash with 100 cc. of hot water. Cool the filtrate and acidify with conc. HCl. *o*-Benzoyl benzoic acid is precipitated. Stir thoroughly and allow to stand for ½ hour. Filter and wash the residue with 50 cc. of cold water. Dry the residue.

Add 5 g. of the dry *o*-benzoyl benzoic acid to 35 g. of conc. H_2SO_4. Heat for 1 hour on an oil bath at 150°. Cool and cautiously pour the mixture on to ice and stir. The resulting anthraquinone precipitates. Filter, wash with hot water, dry and purify by sublimation as indicated in the diagram below.

Reduction and reoxidation.—Boil 0.1 g. of powdered anthraquinone with 30 cc. of 5 per cent NaOH solution and 0.2 g. of zinc dust. A red coloration is produced. This is due to the formation of .

Filter this red liquid into a small beaker and stir. The red color disappears, owing to oxidation by the air. Anthraquinone is again formed.



Laboratory

Commercial

Fig. 72.—Sublimation Apparatus.

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EXPT. 40. NAPHTHALENE, ANTHRACENE AND THEIR DERIVATIVES

1. Write the formula for (*a*) naphthalene picrate and (*b*) anthracene picrate.

2. Write the equation for the reaction in Expt. (*e*).

3. Write the equation for the reaction in Expt. (*f*).

4. Write the equations for the reactions in Expt. (*g*).

5. Why is muslin, instead of filter paper, used for filtration in Expt. (*g*)?

6. Write the equations for the reactions in Expt. (*h*).

7. What is the present commercial process for the preparation of phthalic anhydride?

8. Write the equations for the reactions in Expt. (*k*).

9. Compare the reactions studied in this experiment with those studied in the experiment on benzene and its derivatives.

10. Compare the laboratory sublimation apparatus with the commercial form (Fig. 72) and indicate their corresponding parts.

11. Why are steam or oil coils used in preference to direct fire in the commercial sublimation apparatus shown in Fig. 72?

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EXPT. 41. DYES

AZO DYE

(*a*) Refer to Expts. (*i*) (p. 148); (*j*) (p. 148); (*k*) (p. 148).

NITRO DYE

(*b*) Refer to Expt. (*h*) (p. 151).

TRIPHENYLMETHANE DYE

(*c*) **Malachite Green.**—1. Preparation of the leuco-base: Put 9 g. of fused zinc chloride in a large evaporating dish and heat with a low flame until bubbling ceases. Then, by tilting the dish as the zinc chloride cools, spread it out so that it covers a large area when cold. Then add 20 g. of dimethylaniline and 8 g. of benzaldehyde. Cover with a watch glass. Place the dish on a water bath and heat for 4–5 hours, stirring frequently with a glass rod which is left in the dish. Loosen the solid reaction product with boiling water and transfer to a liter round-bottom flask. Remove the excess dimethylaniline by steam distillation. Allow the contents of the flask to cool and decant the liquid. Wash the pasty mass adhering to the side of the flask with cold water and then dissolve it in hot alcohol. Filter into an evaporating dish, cover with a watch glass, and set the filtrate aside until the next laboratory period. The white solid which separates is the leuco-base (white-base) of malachite green. Filter and dry the crystals on filter paper.

NOTE:—On a commercial scale, conc. HCl is used instead of zinc chloride.

2. Oxidation of the leuco-base: Dissolve 5 g. of the dried leuco-base in a solution of 4 cc. of conc. HCl in 15 cc. of water. Pour this solution into a liter beaker containing 400 cc. of water and add 2 cc. of glacial acetic acid. Stir. Cool the solution by adding ice. Then add, slowly and with constant stirring, the thin paste of lead dioxide (as prepared below). Allow to stand for 5 minutes and then add a solution of 5 g. of sodium sulfate in 25 cc. of water. Filter and treat the filtrate with a solution of 4 g. of zinc chloride in 10 cc. of water. Add solid NaCl and stir until no more will dissolve. Filter off the precipitated zinc chloride salt of the dye by suction. Purify by redissolving in hot water, cooling and salting out again. Filter once more and dry the dye on a porous plate.

NOTE:—Make the lead dioxide paste by dissolving 6 g. of lead acetate in 30 cc. of water. Heat, not quite to boiling, and slowly add a filtered solution of 20 g. of bleaching powder in 300 cc. of water. The addition is stopped when the precipitate becomes dark brown and a test portion of the clear liquid no longer gives a precipitate with the bleaching powder solution. Allow to settle, decant the liquid and wash the precipitate 3 times with water. Filter by suction. Preserve it as a paste in a stoppered bottle.

3. Precipitation of the color-base: To about 1 g. of the malachite green dye as prepared above add NH_4OH until the green color is discharged. **Result:**—

The residue is the color-base. Wash three times with water by decantation. Add a solution of 0.5 g. of oxalic acid in 15 cc. of water. **Result:**—

ANTHRAQUINONE DYE

(*d*) **Alizarin.**—Cautiously and with continuous shaking, fuse in a hard-glass test tube 1 g. of sodium β-anthraquinonesulfonate, 3 g. of powdered sodium hydroxide and 0.2 g. of potassium chlorate (no more, otherwise serious explosion results) until a violet-colored product is produced. Cool and extract with water. The aqueous solution should be a deep violet color. Acidify with dilute HCl solution (1 : 10). **Result:**—

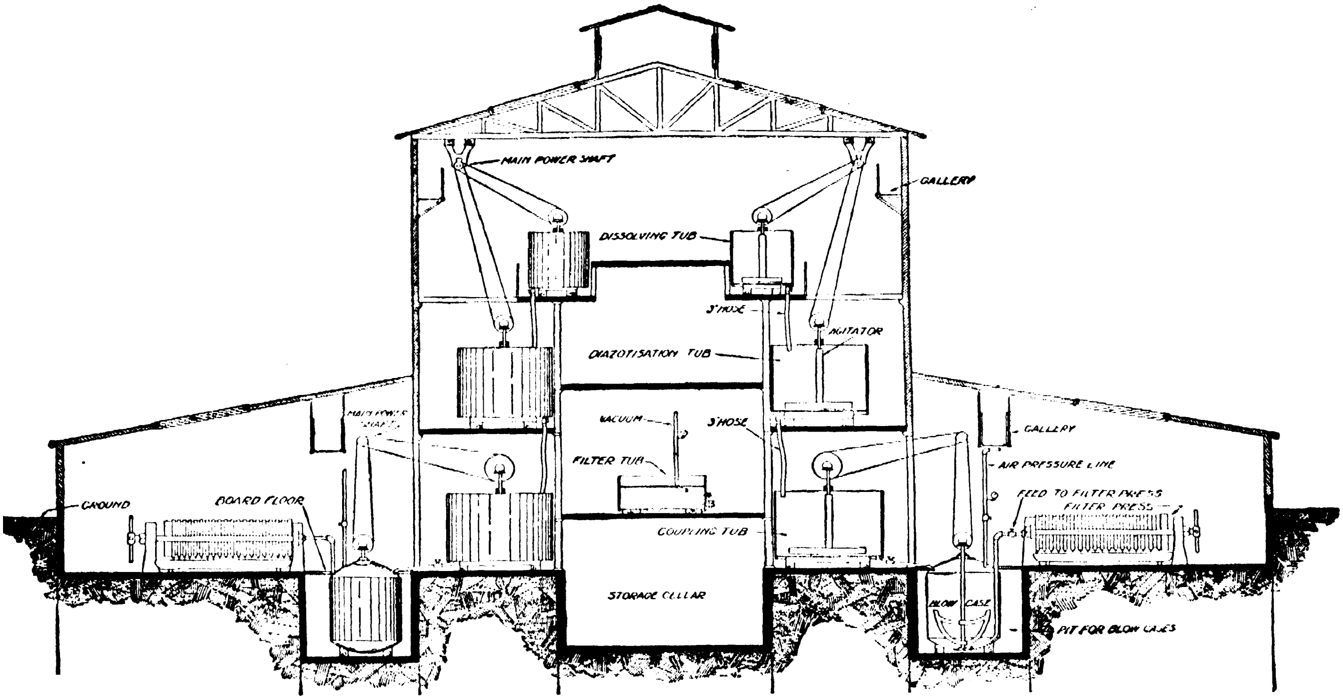

FIG. 73.—Azo Dye Plant.

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EXPT. 41. DYES

1. What are (*a*) the chromophore and (*b*) the auxochrome groups of the dyes referred to in Expt. (*a*) and Expt. (*b*)?

2. Define and illustrate the following terms used in the preparation of azo dyes:—(*a*) active component; (*b*) passive component; and (*c*) coupling.

3. What is the function of the zinc chloride in Expt. (*c*)1?

   Why is HCl preferable?

4. Write the equation for the reaction in Expt. (*c*)1.

5. Why is an excess of dimethylaniline used?

6. Write the equation for the oxidation of the leuco-base in Expt. (*c*)2.

7. What is the function of the Na_2SO_4?

8. What is the function of the $ZnCl_2$?

9. What is the function of the NaCl?

10. What would result if too much PbO_2 were added?

11. Why do you wash the PbO_2 precipitate three times with water?

12. Write the equations for the reactions in Expt. (*c*)3.

13. What is the appearance and color of the color-base?

14. Write the equations for the reactions in Expt. (*d*).

15. What is the function of the $KClO_3$ in Expt. (*d*)?

16. Write the quinoid structure for malachite green.

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EXPT. 42. DYES—METHODS OF APPLICATION

General Directions

For all the experiments on dyeing use distilled water. Boil samples of cloth (4 cm. × 1 cm.) in water or dilute soap solution or 3 per cent HCl solution for 10 minutes in order to remove foreign materials such as sizing, etc., adhering to the surface of the cloth. Then rinse several times with distilled water. Finally squeeze out as much water as possible. Use these treated samples for the dyeing experiments.

Direct Cotton Dyes

Dyes that can be applied to cotton directly (without mordants) are called direct cotton dyes. These dyes are also direct for silk and wool but, owing to the superiority of acid and basic colors with animal fibers (silk, wool, etc.), they are not used to any extent for dyeing these types of fibers. The action of this class of dyes with the fiber seems to be mechanical rather than chemical. Sodium chloride or sodium sulfate is usually added to the bath to decrease the solubility of the dye and to exhaust the dye from the bath. Sodium carbonate is added to the bath to increase the fastness of the dye and to give better exhaustion.

(*a*) **Dyeing with Congo Red.**—To 0.4 g. of Congo red dissolved in 200 cc. of water add a solution of 0.3 g. of Na_2CO_3 in 30 cc. of water and a solution of 0.4 g. of NaCl in 10 cc. of water. Heat this mixture to about 70° and immerse in it a sample of cotton cloth. Stir and after 10 minutes remove the cloth, wash thoroughly with water, and hang up to dry. By means of gummed paper attach the dried sample in the space below.

(*b*) **Action of Certain Salts.**—Make a solution of 0.1 g. of Congo red in 20 cc. of water. Divide into two portions. To one portion add 5 cc. of a 10 per cent solution of $CaCl_2$. **Result:**—

To the other portion add 5 cc. of a 10 per cent solution of $MgSO_4$. **Result:**—

Hard water should not be used for dyeing. Why?

Acid Dyes

These dyes are mainly used for the dyeing of wool and silk, and only to a limited extent for cotton or other vegetable fibers. Since animal fibers are of a protein nature they contain acid as well as basic groups. The presence of acid groups makes it possible for them to unite with basic compounds.

Animal fibers absorb acid dyes readily from the bath. In preparing the dye bath, Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) and enough dye to give the desired color depth are used. Glauber's salt prevents the dye from being too rapidly absorbed by the fiber. Such a substance, if used to prevent an uneven distribution of the dye, is called a "leveling agent." The H_2SO_4 is used to liberate the dye as free acid so that it may more readily combine with the basic component of the fiber, and to increase the exhaustion of the bath.

(*c*) **Dyeing with Acid Colors.**—For this experiment acid red, acid magenta, acid yellow, acid green, acid fast green, etc. may be used. To 200 cc. of water add 5 g. of Glauber's salt, 4 g. of H_2SO_4 and 1 g. of the dye. Stir well and heat to 60°. Place in this bath prepared squares of cotton, wool and silk. Stir occasionally and heat the bath gradually just to the boiling point. (Do not boil.) After ½ hour remove the samples of cloth, squeeze out the liquid, and rinse well with water until the water ceases to be colored. Then squeeze out the water and dry. Attach the dyed samples.

BASIC DYES

These are direct dyes for wool and silk but are not used to dye cotton and other vegetable fibers directly. Cotton is dyed with basic dyes by using mordants of acid character. The basic groups of this class of dyes unite with the acid components in the animal fiber.

Since basic dyes are absorbed very rapidly by animal fibers in neutral solutions, acetic acid is usually added to the bath to slow up the rate of dyeing and thus prevent an uneven distribution of the dye in the fiber. Glauber's salt is also introduced into the bath to act as a "leveling agent." The basic dyes produce bright shades on silk and wool but are not fast.

Tannic acid with tartar emetic is commonly used as a mordant in dyeing vegetable fibers with this class of dyes. The cloth is placed in a solution of tannic acid until thoroughly impregnated. It is then placed in a solution of tartar emetic. An insoluble antimonyl tannate is formed. The mordanted cloth is then placed in the dye bath.

(*d*) **Direct Dyeing with Basic Dyes.**—For this experiment use the malachite green you prepared. Crystal violet, magenta, safranine, auramine, brilliant green, etc. may also be used.

To 200 cc. of water add 5 g. of Glauber's salt, 2 g. of acetic acid, and 1 g. of the dye. Heat to 40°. Introduce prepared samples of cotton, wool and silk. Gradually raise the temperature to 85°, stirring occasionally. After ½ hour remove the pieces of cloth, rinse thoroughly, squeeze out the water, and dry. Attach the dyed samples.

(*e*) **Basic Dye with a Mordant.**—Dissolve 0.4 g. of tannic acid in 50 cc. of water. Make a tartar emetic solution by dissolving 0.2 g. in 150 cc. of water. Also make a malachite green solution by dissolving 0.5 g. of the dye in 200 cc. of water.

Into the tannic acid solution put a sample of cotton cloth and allow it to stand for about 10 minutes. Remove the cloth and place it in the tartar emetic solution. After about 10 minutes place the cloth in the malachite green solution and gradually heat to about 80°. Stir occasionally. After 15 minutes remove the cloth, rinse thoroughly and dry. Compare this sample with the unmordanted piece of cotton. **Result:**—

Attach the dyed sample.

VAT DYE

Many dyestuffs are insoluble in the ordinary solvents. The usual methods of application cannot be employed with such dyes. Many of these insoluble dyes can be reduced and converted into "leuco" compounds which are soluble and adhere to the fiber. These "leuco" compounds on exposure to the air are converted to the original compounds. Such dyes are called "vat dyes." Indigo belongs to this class.

(*f*) **Dyeing with Indigo.**—Place 1 g. of indigo paste (20 per cent) in a 200 cc. beaker. Add 25 cc. of a 10 per cent $NaOH$ solution. Stir well to produce a uniform suspension. Add 75 cc. of water and heat to 45°. Gradually add 5 g. of sodium hyposulfite (hydrosulfite) ($Na_2S_2O_4$). Stir until a greenish-yellow colored solution is obtained with a film of indigo on the surface. Immerse a piece of cotton in the reduced indigo solution (leuco-indigo) and agitate for 5 minutes. Keep the temperature at 40°. Remove the cotton from the bath, squeeze out the excess dye and expose it to the air for about 15 minutes. When the cotton is removed from the bath, it should have a yellowish-green color; on exposure it turns blue. Wash well in running water. Squeeze out the water and hang up to dry. Attach the dyed sample.

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EXPT. 43. HETEROCYCLIC COMPOUNDS

THIOPHENE

(*a*) **Test for Thiophene.**—Repeat Expt. (*d*) (p. 131). This is known as the indophenin test. **Result:—**

FURFURAL

(*b*) **Preparation.**—In a 500 cc. distilling flask place about 50 g. of corn cobs (ground to the size of peas), 200 cc. of 10 per cent H_2SO_4, and 30 g. of NaCl. Shake well. Attach a condenser and distill over about 25 cc. Note the odor. The distillate contains furfuraldehyde.

(*c*) **Color Test.**—To 5 cc. of the distillate add 1 drop of aniline and 5 drops of conc. HCl. **Result:—**

PYRIDINE

(*d*) **Action toward Litmus Papers.**—Shake 5 drops of pyridine with 5 cc. of water. Test the solution with litmus papers. **Results:—**

(*e*) **Basic Action of Pyridine.**—To 5 cc. of an aqueous solution of pyridine add 2 cc. of a 10 per cent ferric chloride solution. **Result:—**

(*f*) **Action of Pyridine toward Oxidizing Agents.**—Dissolve 5 drops of pyridine in 5 cc. of water. Add 0.5 g. of sodium dichromate and 2 cc. of conc. H_2SO_4. Heat. **Result:—**

(*g*) **Pyridine and Methyl Iodide.**—Warm 2 cc. of pyridine with 2 cc. of methyl iodide until boiling begins. Cool the product in ice. **Result:—**

QUINOLINE

(*h*) **Preparation (Skraup's Reaction).**—Into a 100 cc. flask pour 6 cc. of aniline, $\frac{1}{2}$ cc. of glycerol, 8 cc. of H_2SO_4 and 4 cc. of nitrobenzene. Attach a reflux condenser and shake. Heat on a sand bath with a low flame until ebullition *just* starts. Then remove the burner, wait until the reaction has moderated, and continue heating for 10 minutes. Cool, pour the mixture into water and neutralize with a 10 per cent NaOH solution. Note the odor.

The liquid contains quinoline and the excess of nitrobenzene, aniline, etc.

(*i*) **Properties of Quinoline.**—1. Action toward litmus papers: To 3 drops of quinoline add 5 cc. of water. Shake and test the solution with litmus papers. **Results:—**

2. Action of quinoline and acids: To 1 cc. of quinoline add 5 cc. of a 20 per cent HCl solution. **Result:—**

Now neutralize with a 10 per cent NaOH solution. **Result:—**

URIC ACID

(*j*) **Murexide Reaction.**—To 0.2 g. of uric acid add 5 drops of conc. nitric acid. Evaporate to dryness on a water bath. **Result:—**

Cool. To one-half of the residue add a few drops of ammonium hydroxide. **Result:—**

To the remainder of the residue add a few drops of a 10 per cent NaOH solution. **Result:—**

(*k*) **Reducing Action of Uric Acid.**—1. Reduction of $AgNO_3$: Dissolve 0.2 g. of uric acid in 20 per cent Na_2CO_3 solution. Place a few drops of this solution on a filter paper moistened with silver nitrate solution. **Result:—**

2. Reduction of Fehling's solution: To about 5 cc. of Fehling's solution add about 0.1 g. of uric acid. Boil for 5 minutes. **Result:—**

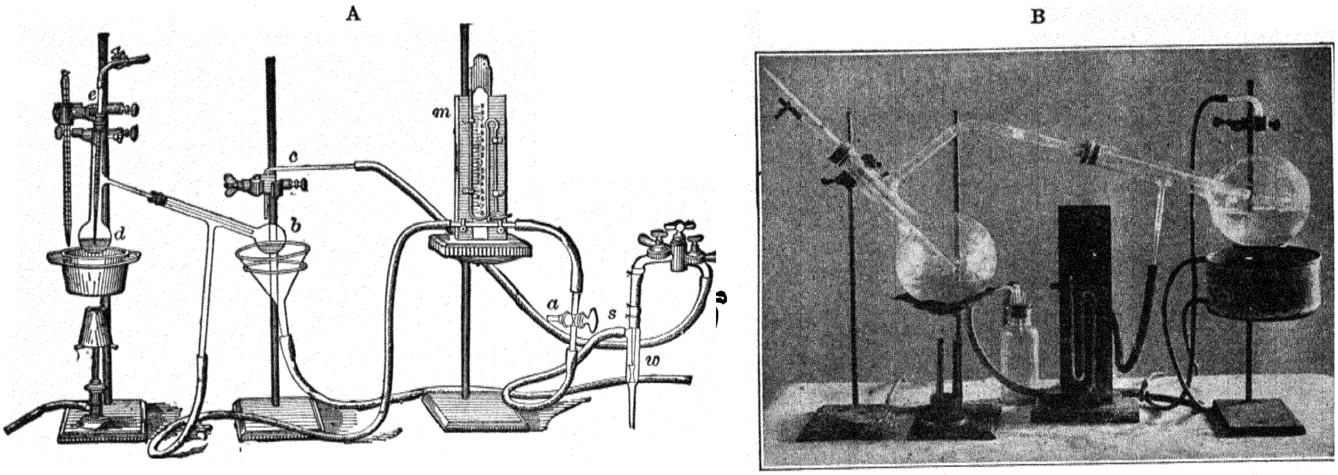

FIG. 74.—Laboratory Vacuum Distillation Apparatus.

The liquid for distillation is placed in *d*. The glass tube *e* is drawn out to a very fine point and made to dip into the liquid. A thermometer may be placed in this tube. During distillation, the tube *e* permits a fine stream of air to be kept bubbling through the liquid to prevent "bumping." The receiver *b* is kept cool by a stream of water from *c*. *m* is a mercury manometer; *a* is a three-way stopcock which permits access of air to the apparatus for "breaking" the vacuum; *s* is the side tube of the water-pump *w*. All rubber connections are made with pressure tubing.

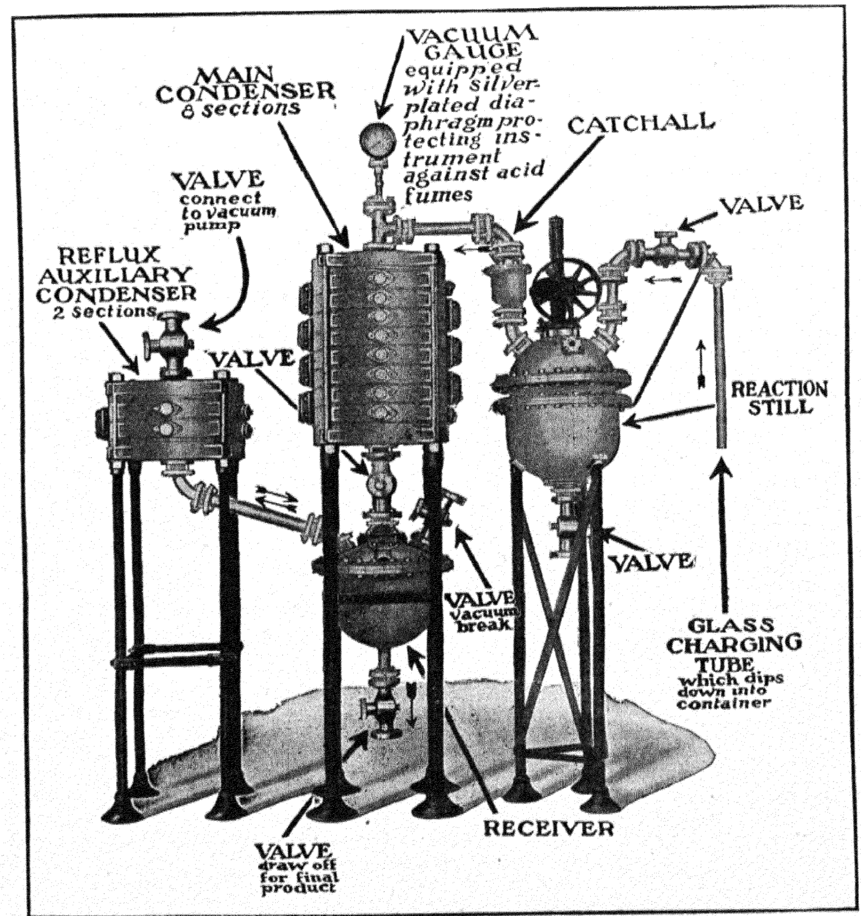
MAIN CONDENSER 8 sections
VACUUM GAUGE equipped with silver-plated diaphragm protecting instrument against acid fumes
CATCHALL
VALVE connect to vacuum pump
VALVE
REFLUX AUXILIARY CONDENSER 2 sections
VALVE
REACTION STILL
VALVE
VALVE Vacuum break
GLASS CHARGING TUBE which dips down into container
RECEIVER
VALVE draw off for final product

FIG. 75.—Vacuum Distillation.

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EXPT. 43. HETEROCYCLIC COMPOUNDS

1. With what compound is thiophene nearly always present? How is it removed?

2. What class of compounds is present in corn cobs which produces furfural?

3. What is the function of the H_2SO_4 and NaCl in Expt. (*b*)?

4. Write the equation for the formation of furfuraldehyde from an aldopentose.

5. What property of pyridine does Expt. (*d*) show?

6. Explain the reaction produced in Expt. (*e*).

7. What does Expt. (*f*) show in regard to the stability of pyridine?

8. Write the equation for the reaction in Expt. (*g*) and name the compound produced.

9. Mention an important use for pyridine.

10. Write the equations for the reactions in Expt. (*h*).

What is the function of the nitrobenzene?

11. Why is the NaOH solution added in Expt. (*h*)?

12. Write the equations for the reactions in Expt. (*i*)2.

13. What is meant by "vacuum distillation"?

Why do we resort to this type of distillation?

14. From a study of the parts of the apparatus shown in Figs. 74A and 74B, indicate the corresponding parts of Fig. 75.

15. Why are autoclaves constructed with thick walls?

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EXPT. 44. ALKALOIDS

Warning: Nux Vomica is poisonous.

(*a*) **Extraction of Strychnine and Brucine from Nux Vomica.**—Put 4 g. of powdered nux vomica into a 100 cc. flask. Add 30 cc. of ether, 10 cc. of chloroform, 30 cc. of alcohol and 1 cc. of ammonium hydroxide (10 per cent). Shake frequently during 1 hour. Decant the supernatant liquid into a small separatory funnel. Add 20 cc. of H_2SO_4 (5 per cent), shake thoroughly and draw off the acid layer. Filter. Pour the filtrate into a small separatory funnel and add ammonium hydroxide in slight excess. Add 15 cc. of chloroform and shake thoroughly. Draw off the chloroform layer. Filter, if necessary. Evaporate the chloroform solution to dryness on a water bath. The residue contains strychnine and brucine.

(*b*) **Detection of Strychnine and Brucine when Together.**—Add 5 drops of conc. H_2SO_4 to the residue from the chloroform extract. Add 5 drops of water. To 5 drops of this mixture add a fragment of KNO_3 and stir. Red coloration changing to yellow shows the presence of brucine. Now add a small crystal of $K_2Cr_2O_7$ and stir. Note the blue or reddish-violet coloration around the crystal. This shows the presence of strychnine.

(*c*) **Alkaloid Precipitants.**—Make up a solution of 0.1 g. of quinine sulfate in 10 cc. of water. Pour 2 cc. of this solution into each of five test tubes. To the first test tube add one drop of iodine in KI solution; to the second, a drop of a solution of phosphomolybdic acid in nitric acid; to the third, a drop of potassium mercuric iodide solution; to the fourth, a drop of picric acid solution; and to the fifth, a drop of a tannic acid solution. **Results:—**

(*d*) **The More Important Alkaloids and their Sources:—**

Coniine—seeds of spotted hemlock
Nicotine—tobacco leaves
Piperine—pepper
Atropine—deadly nightshade
Cocaine—coca leaves
Quinine—cinchona bark
Cinchonine—cinchona bark
Strychnine—seeds of nux vomica
Brucine—seeds of nux vomica
Morphine—opium
Narcotine—opium
Codeine—opium
Pilocarpine—leaves of pilocarpus jaborandi
Emetine—ipecac
Caffeine—coffee, tea

Alkaloids respond to many color reactions with various reagents. These color reactions are mainly utilized to identify them. For experimental details concerning many of these tests, the student is referred to the following books:—

PRICE AND TWISS—Practical Organic Chemistry.
STEEL—Laboratory Manual of Organic Chemistry for Medical Students.
TITHERLEY—A Laboratory Course in Organic Chemistry.
U. S. DISPENSATORY.

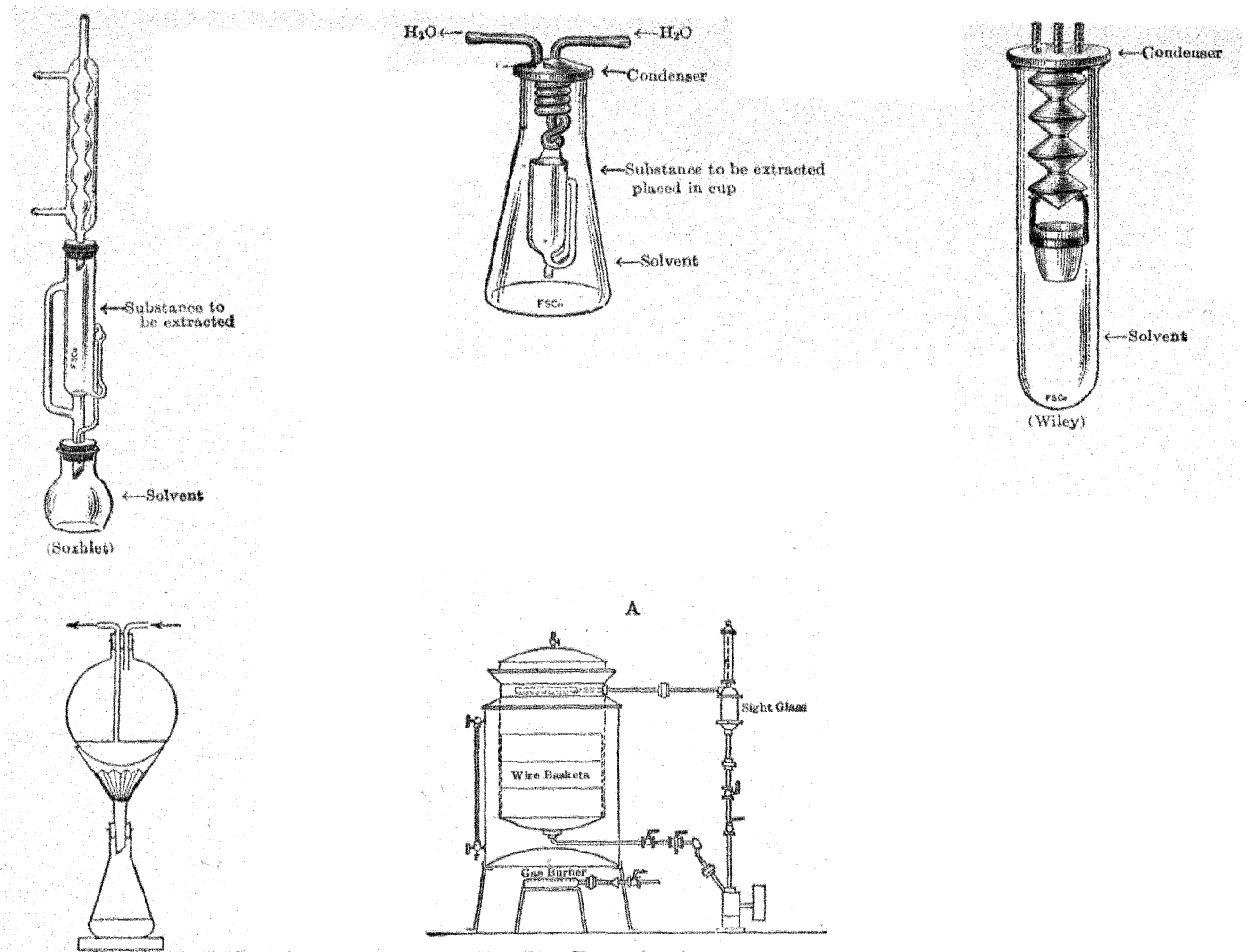

Fig. 76.—Extraction Apparatus.

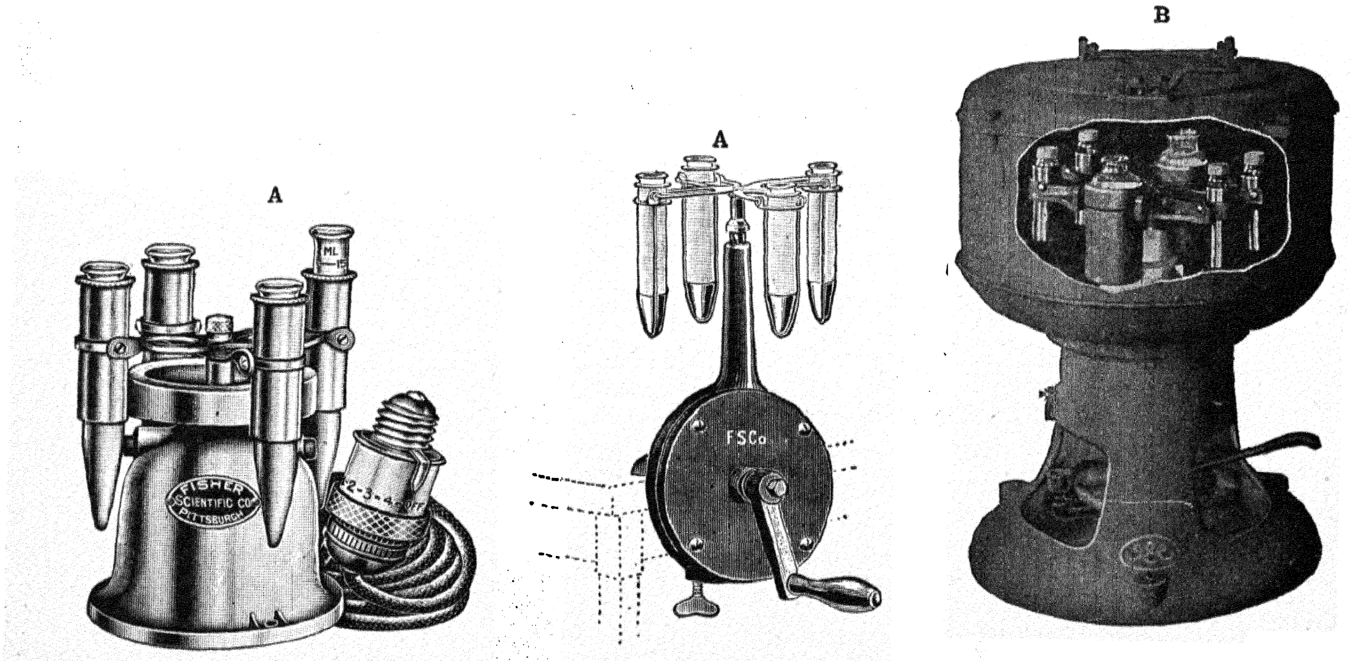

Fig. 77.—Centrifuges.

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EXPT. 44. ALKALOIDS

1. In combination with what class of compounds do the alkaloids occur in nature?

2. What typical heterocyclic groups are generally present in alkaloids?

3. Give reasons for each step in Expt. (*a*).

4. Name the alkaloidal precipitants.

   What other class of compounds already studied is precipitated by them?

5. List the physiological properties of a few well-known alkaloids.

6. Why are the alkaloids administered usually in the form of sulfates, hydrochlorides, nitrates, phosphates or other salts?

7. Discuss the general scheme used for the extraction of alkaloids from plants.

8. Give some practical uses for the centrifuges shown in Fig. 77.

9. Why are the materials to be extracted placed in baskets in the apparatus shown in Fig. 76A?

APPENDIX

1. Laboratory Books in Organic Chemistry

Adams, Conant, Clarke, Kamm, Marvel, Gilman—Organic Syntheses. (Wiley.)
Adams and Johnson—Elementary Laboratory Experiments in Organic Chemistry. (Macmillan.)
Adkins and McElvain—Practice of Organic Chemistry. (McGraw-Hill.)
Barnett—Preparation of Organic Compounds. (Blakiston.)
Bender-Erdmann—Chemischer Präparatenkunde. Vol. 2 (Enke, Stuttgart.)
Cain and Thorpe—The Synthetic Dyestuffs and Intermediate Products. (Griffin, London.)
Cohen—Practical Organic Chemistry. (Macmillan.)
Coleman and Arnall—Preparation and Analysis of Organic Compounds. (Churchill, London.)
Cook—Laboratory Experiments in Organic Chemistry. (Blakiston.)
Cumming, Hopper and Wheeler—Systematic Organic Chemistry. (Van Nostrand.)
Elbs—Übungsbeispiele für die elektrolytische Darstellung Chemischer Präparate. (Knappe, Halle.)
Fischer—Preparation of Organic Compounds. (Van Nostrand.)
Fisher—Laboratory Manual of Organic Chemistry. (Wiley.)
Fourneau—Organic Medicaments and Their Preparation. (Blakiston.)
Garrett and Harden—Practical Organic Chemistry. (Longmans.)
Gattermann and Wieland—Laboratory Methods of Organic Chemistry. (Macmillan.)
Hawk and Bergeim—Practical Physiological Chemistry. (Blakiston.)
Heidelberger—Advanced Laboratory Manual of Organic Chemistry. (Chemical Catalog.)
Henle—Anleitung für das Organisch-chemische Praktikum. (Akademische Verlagsgesellschaft, Leipzig.)
Holleman and Walker—Laboratory Manual of Organic Chemistry. (Wiley.)
Houben and Weyl—Die Methoden der Organischen Chemie. (Thieme, Leipzig.)
Jones—Laboratory Outline of Organic Chemistry. (Century.)
Kellar—Practical Organic Chemistry. (Oxford.)
Lassar-Cohn and Oesper—Organic Laboratory Methods. (Williams and Wilkins.)
Lassar-Cohn—Applications of Some General Reactions to Investigations in Organic Chemistry. (Wiley.)
Levy—Organische Präparata. (Enke, Stuttgart.)
Moore—Experiments in Organic Chemistry. (Wiley.)
Norris—Experimental Organic Chemistry. (McGraw-Hill.)
Noyes—Organic Chemistry for the Laboratory. (Chemical Publishing.)
Orndorff—Laboratory Manual in Organic Chemistry. (Heath.)
Porter, Stewart and Branch—The Methods of Organic Chemistry. (Ginn.)
Price and Twiss—Practical Organic Chemistry. (Longmans.)
Steel—Laboratory Manual of Organic Chemistry for Medical Students. (Wiley.)
Sudborough and James—Practical Organic Chemistry. (Van Nostrand.)
Titherley—A Laboratory Course in Organic Chemistry. (Van Nostrand.)
Vanino—Handbuch der Präparativen Chemie. (Enke, Stuttgart.)
West—Experimental Organic Chemistry. (Globe Book.)
Williams and Brewster—Laboratory Manual of Organic Chemistry. (Van Nostrand.)

2. Reference Books for Use in the Laboratory

An Inorganic Chemistry Book.
Laboratory Books of Organic Chemistry.
Text-Books of Elementary Organic Chemistry.
Atack—The Chemist's Year-Book. (Longmans, Green.)
Beilstein's Handbuch der Organischen Chemie. (Springer, Berlin.)
Hodgman and Lange—Handbook of Chemistry and Physics. (Chemical Rubber Publishing Co., Cleveland, O.)
International Critical Tables. (McGraw-Hill.)
Kamm—Qualitative Organic Analysis. (Wiley.)
Mulliken—Identification of Pure Organic Compounds. (4 vols.) (Wiley.)
Olsen—Chemical Annual. (Van Nostrand.)
Richter—Organic Chemistry. (3 vols.) (Blakiston.)
Seidell—Solubilities of Inorganic and Organic Substances. (Van Nostrand.)

3. Atomic Weights of a Few Elements

Bromine	Br	79.92
Calcium	Ca	40.07
Carbon	C	12
Chlorine	Cl	35.46
Hydrogen	H	1.008
Iodine	I	126.92
Nitrogen	N	14.008
Oxygen	O	16
Phosphorus	P	31.04
Potassium	K	39.1
Sodium	Na	23
Sulfur	S	32.06

4. Specific Gravities and Boiling Points of a Number of Common Organic Liquids

	sp. gr.	b.p. °C. Corrected.
Acetic acid	1.049^{20}_{4}	119
Acetic anhydride	1.082^{20}_{4}	139.5
Acetone	$.79^{15}_{4}$	56.5
Aniline	1.021^{25}_{25}	184.4
Benzene	$.878^{20}_{4}$	80.4
Carbon disulfide	1.292^{0}_{4}	46.2
Carbon tetrachloride	1.583^{25}_{4}	76.7
Chloroform	1.498^{15}_{4}	61.2
Ethyl acetate	$.900^{20}_{4}$	77.1
Ethyl alcohol	$.785^{25}_{4}$	78.4
Ethyl ether	$.719^{15}_{15}$	35
Glycerol	1.260^{20}_{4}	291
Methanol	$.796^{15}_{15}$	64.6
Nitrobenzene	1.198^{25}_{4}	210.8
Phenol	1.067^{35}_{35}	182.6
Toluene	$.861^{25}_{4}$	110.7

5. Special Reagents

Ammonium Molybdate Solution (Phosphorus).—To a mixture of 135.5 cc. of cold distilled water and 72 cc. of NH_4OH (sp. gr. 0.90), add 50 g. of MoO_3 and stir till solution is complete. Slowly add this solution with constant stirring to a mixture of 244.5 cc. of HNO_3 (sp. gr. 1.42) and 574 cc. of water. Allow the mixture to stand for twenty four hours and decant the clear liquid into a bottle.

Bromine Water (Unsaturation).—Shake 25 cc. of bromine with 1 liter of distilled water.

Fehling's Solution (Carbohydrates–Aldehydes).—Solution A.—Dissolve 34.65 g. of copper sulfate in 500 cc. of distilled water.

Solution B.—Dissolve 65 g. of sodium hydroxide and 173 g. of Rochelle salt in 500 cc. of distilled water.

Use equal volumes of A and B.

Hopkins-Cole Reagent or Glyoxylic Acid Reagent (Proteins).—Cover 10 g. of magnesium with distilled water. Slowly add 250 cc. of saturated oxalic acid, cooling under the tap. Filter off the insoluble magnesium oxalate. Acidify the filtrate with acetic acid, and dilute to 1 liter with distilled water. The solution should be kept in a closed bottle containing a little chloroform.

Iodine in Potassium Iodide (starch, ethyl alcohol, acetone, etc.).—Dissolve 5 g. of iodine and 25 g. of potassium iodide in 100 cc. of distilled water. Dilute to any concentration desired.

Millon's Reagent (Proteins).—Dissolve 100 g. of mercury in 142 cc. of conc. HNO_3. Add 280 cc. of distilled water. Filter if necessary. The solution contains $HgNO_3$, $Hg(NO_3)_2$, HNO_3 and HNO_2.

Molisch's Reagent (Carbohydrates).—10 per cent solution of α-naphthol in alcohol or chloroform.

Nylander's Solution (Carbohydrates).—Dissolve 40 g. of Rochelle salt and 20 g. of bismuth subnitrate in 1000 cc. of 8 per cent NaOH solution. Cool and filter.

Phenolphthalein Solution (indicator).—1 per cent of phenolphthalein in alcohol.

Phloroglucinol Solution (Pentosans).—3 per cent phloroglucinol solution in alcohol. Keep in amber-colored bottle.

Phosphomolybdic Acid (Alkaloids).—Dissolve 10 g. of phosphomolybdic acid in 100 cc. of HNO_3 (1 : 3) Filter it if necessary.

Phosphotungstic Acid (Proteins).—A solution of 2 per cent phosphotungstic acid in 5 per cent H_2SO_4.

Potassium Mercuric Iodide (Alkaloids).—Dissolve 13.5 g. of $HgCl_2$ and 49.8 g. of KI in 1 liter of distilled water.

Schiff's Reagent (Aldehyde).—Dissolve 1 g. of rosaniline (fuchsine) in 250 cc. of boiling water. Cool and pass in sulfur dioxide from a cylinder or generator until the solution becomes pale yellow in color. Allow it to stand overnight. Dilute to 1 liter. Keep the solution in an amber-colored bottle.

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